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Incineration and Treatment of Hazardous Waste
Proceedings of the Annual Research Symposium
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16. ABSTRACT

The Thirteenth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, May 6-8, 1987. The purpose of the Symposium was to present the latest significant research findings of ongoing and recently completed projects funded by the Hazardous Waste Engineering Research Laboratory (HWERL) to persons concerned with hazardous waste management.

These proceedings are for Session A, Hazardous Waste Land Disposal, Session B, Hazardous Waste Incineration and Treatment, and Session C, HWERL Posters. Papers presented by Symposium speakers and poster presentation Abstracts are compiled. Land Disposal subjects discussed included landfill design and operation, waste leaching and analyses, pollution migration and control, personnel protection, surface impoundments, flexible membrane liners, remedial action techniques and underground mine disposal. Incineration and treatment subjects included combustion of hazardous wastes in incinerators, boilers and industrial processes, field evaluations, treatment options and innovative processes for hazardous waste destruction.

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at Cincinnati, Ohio, May 6-8, 1987

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FOREWORD

As hazardous waste continues to be one of the more prominent environmental concerns to the people of the United States and other countries throughout the world, there are continuing needs for research to characterize problems and develop and evaluate alternatives to addressing those problems. The programs of the Hazardous Waste Engineering Research Laboratory (HWERL) are designed to contribute to satisfying these research needs.

These Proceedings from the 1987 Symposium provide the results of projects recently completed by HWERL and current information on other projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

ABSTRACT

The Thirteenth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, May 6 through May 8, 1987. The purpose of this Symposium was to present the latest significant research findings of ongoing and recently completed projects funded by the Hazardous Waste Engineering Research Laboratory (HWERL) to persons concerned with hazardous waste management.

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TECHNICAL RESOURCE DOCUMENTS AND TECHNICAL HANDBOOKS FOR HAZARDOUS WASTES MANAGEMENT

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and
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ABSTRACT

The Environmental Protection Agency is preparing a series of Technical Resource Documents (TRD's) and Technical Handbooks to provide best engineering control technology to meet the needs of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) respectively. These documents and handbooks are basically compilation of research efforts of the Land Pollution Control Division (LPCD) to date. The specific areas of research being conducted under the RCRA land disposal program relate to laboratory, pilot and field validation studies in cover systems, waste leaching and solidification, liner systems and disposal facility evaluation. The specific areas of research being conducted under the CERCLA uncontrolled waste sites (Superfund) program relate to pilot and field validation studies in barriers, waste storage, waste treatment, modeling and postclosure evaluation. The technical resource documents are intended to assist both the regulated community and the permitting authorities, as well as support the RCRA Technical Guidance Documents prepared by EPA's Office of Solid Waste (OSW). The technical handbooks provide the EPA Program Offices and Regions, as well as the states and other interested parties, with the latest information relevant to remedial actions.

INTRODUCTION

Land disposal of hazardous waste is subject to the requirements of Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976 and to the 1984 Amendments to this Act. This Act requires that the treatment, storage, or disposal of hazardous waste be carried out in accordance with RCRA regulations. Owners and operators of new facilities must apply for and receive a RCRA permit before beginning operation of such a facility.

The clean up or containment technology associated with remedial action at an existing uncontrolled hazardous waste is subject to the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund). This Act requires evaluation of remedial action clean up technologies.

To meet the Control Technology aspects of RCRA and CERCLA as related to Land Disposal Facilities, the research program has relied heavily on the containment aspects of the wastes at the facility or site. The containment aspects for waste disposal onto the land needs to address the development of performance and operational standards for new waste disposal facilities (RCRA sites) and the containment or destruction of pollutants emanating from existing waste disposal facilities (CERCLA sites). The control technology research approach being pursued by the USEPA is to develop an improved data base so that current waste disposal practices can be upgraded by developing proper site selection criteria and control technology for the establishment of new waste disposal facilities, and to develop improved containment technology for existing waste disposal sites by minimizing pollutant generation and release to the environment.

The development of proper control technology for new (RCRA) waste disposal facilities will combine information from laboratory, pilot and field validation studies in the research areas of cover systems, waste leaching and solidification liner systems and disposal facility evaluation. Cover systems research is developing and evaluating the effectiveness of various material components (i.e., vegetation, soils, membranes, and drainage blankets) in relation to the cover function of minimizing moisture ingress and gas egress. Waste leaching research is investigating techniques for predicting the composition of actual field leachates from samples of wastes or mixtures of wastes. Waste solidification research is evaluating the effectiveness and performance with time as liners to contain and minimize the release of leachate and gas pollutants to the environment. Disposal facility evaluation research is evaluating effective techniques to ensure that land disposal facilities are built as designed for either permanent disposal or short/ long term storage. Incorporated throughout the research for development of control technology for new waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and regional offices and user communities. The Technical Resource Documents (TRD's) are considered to be primary documents for transferring current RCRA control technologies to the user. The TRD's are being developed and published to assist the permit applicants and permit review officials to assure that the latest containment facility technology is being utilized. The TRD's are to be used in conjunction with the Technical Guidance Documents being prepared by OSW. The documents contain guidance, not regulations or requirements which the Agency believes comply with Design and Operating Requirements and the Closure and Post-Closure Requirements contained in Part 264 of the regulations. The information and guidance presented in these documents constitute a suggested approach for review and evaluation based on good engineering practices. There may be alternative and equivalent methods for conducting the review and evaluation. However, if the results of these methods differ from those of the Environmental Protection Agency's method, they may have to be validated by the applicant.

The development of proper containment technology to upgrade existing (CERCLA) waste disposal facilites will combine information from the above described program for new waste disposal facilities along with pilot and field validation studies in the research areas of barriers, waste storage, waste treatment, modeling, and post-closure evaluation. Barrier research is developing and evaluating insitu control technologies to contain or minimize pollutant releases from uncontrolled sites and to predict performance with time. In-situ control technologies such as slurry walls, grout curtains, cutoff walls, and covers are being evaluated. Waste storage research is evaluating the cost-effectiveness of placing wastes from the clean up of uncontrolled sites into mines or above ground storage facilities. Also, packaging of hazardous wastes in various containers is being investigated. Waste treatment research is evaluating the effectiveness of various techniques for treating the wastes or collected leachates in-place or on-site. Techniques such as stabilization, encapsulation, permeable treatment walls, microbial degradation, and physical/ chemical treatment are being investigated. Modeling technology has been developed for evaluation of remedial action alternatives and will be updated to reflect improved performance, reliability, and cost information from field scale studies, case studies and other research areas. Post-closure research is evaluating the criteria for final site usage once the disposal facility has been remediated. Incorporated throughout the research for development of control technology for existing waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and user communitiess. The Technical Handbooks are considered to be the primary documents for transferring current CERCLA containment technology to the user.

TECHNICAL RESOURCE DOCUMENTS

Eight TRD's have been completed to date. Six of the TRD's are related to landfills, and one document each is related to surface impoundments and land treatment. A listing of these documents is shown below, along with a brief decription, publication number, and the project officer's name is parentheses.

Evaluating Cover Systems for Solid and Hazardous Waste (SW-867)

A critical part of the sequence of designing, constructing, and maintaining an effective cover over solid and hazardous waste sites is the evaluation of engineering plans. This TRD presents a procedure for evaluating closure covers on solid and hazardous wastes sites. All aspects of covers are addressed in detail to allow for a complete evaluation of the entire cover system. There are eleven sequential procedures identified for evaluating engineering plans.

The document describes current technology for landfill covers in three broad areas: data examination, evaluation steps and post-closure plan. The data examination discusses test data review procedure, topographical data review and climatological data review procedures. The evaluation steps include cover composition, thickness, placement, configuration, drainage and vegetation. The post-closure aspects include maintenance and contingency plan evaluation procedures. There are 36 specific steps, regarding the preceding factors, which are recommended to be followed in evaluating a permit for a cover for hazardous waste. *055-000-00228-2 (R.E. Landreth)

Landfill and Surface Impoundment Performance Evaluation (SW-869)

The evaluation of leachate collection systems using compacted clay or synthetic liners to determine how much leachate will be collected and how much will seep through the liner into underlying soils is presented. The adequacy of sand and gravel drain layers, slope, and pipe spacing is also covered. The author has allowed for the widely varied technical backgrounds of his intended audience by presenting, in full, the rigorous mathematics involved in reaching his final equations. Thus, any evaluator can take full advantage of the manual up to the level of his own mathematical proficiency. *055-000-00233-9 (M.H. Roulier)

Lining of Waste Impoundment and Disposal Facilities (SW-870)

This document provides information on performance, selection, and installation of specific liners and cover materials for specific disposal situations, based upon the current state-of-the-art of liner technology and other pertinent technologies. It contains descriptions of wastes and their effects on linings, a full description of various natural and artificial liners, service life and failure mechanisms; installation problems and requirements of liner types, costs of liners and installation, and tests that are necessary for pre-installation and monitoring surveys. A revised version should be available in late 1986. *055-000-00231-2 (R.E. Landreth)

Management of Hazardous Waste Leachate (SW-871)

This document has been prepared to provide guidance for permit officials and disposal site operators on available management options for controlling, treating, and disposing of hazardous waste leachates. It discusses considerations necessary to develop sound management plans for leachate generated at surface impoundments and landfills. Management may take the form of leachate

collection and treatment, or pretreatment of the wastes.
*055-000-00224-0 (S.C. James)

Guide to the Disposal of Chemically Stabilized and Solidified Wastes (SW-872)

The purpose of this TRD is to provide guidance in the use of chemical stabilization/solidification techniques for limiting hazards posed by toxic wastes in the environment, and to assist in the evaluation of permit applications related to this disposal technology. The document addresses the treatment of hazardous waste for disposal or long term storage and surveys the current state and effectiveness of waste treatment technology. A summary of the major physical and chemical properties of treated wastes is presented. A listing of major suppliers of stabilization and solidification technology and a summary of each process is included.
*055-000-00226-6 (R.E. Landreth)

Closure of Hazardous Waste Surface Impoundments (SW-873)

The methods, tests, and procedures involved in closing a surface impoundment are discussed and referenced. Problems related to abandoned methods such as waste removal, consolidating the waste on-site and securing the site as a landfill are also discussed. It is written primarily for staff members in EPA regional offices or state regulatory offices, who are charged with evaluating and approving closure plans for surface impoundments under regulations of the Resource Conservation and Recovery Act of 1976. Methods of assessing site closure considerations are documented.
*055-000-00227-4 (M.H. Roulier)

Hazardous Waste Land Treatment (SW-874)

The objectives of "Hazardous Waste Land Treatment" are to describe current technology and to provide methods for evaluating the performance of an applicant's hazardous waste land treatment facility design. Land treatment is approached comprehensively from initial site selection through final closure, and additional information sources are referenced liberally. Land treatment, which involves using the surface soil as the treatment medium, is already widely practiced by some industries for handling their hazardous wastes.
*055-000-00232-1 (C.C. Wiles)

FUTURE TECHNICAL RESOURCE DOCUMENTS

Additional TRD's now being developed or in planning stages by the Office of Research and Development are included here for reference. A listing of these documents is shown below, along with a brief description and the project officer's name in parentheses.

Soil Properties, Classification and Hydraulic Conductivity Testing

This report is a compilation of available laboratory and field testing methods for the measurement of hydraulic conductivity (permeability) of soils. Background information on soil classification, soil water, and soil compaction are included along with descriptions of sixteen methods for determination of saturated or unsaturated hydraulic conductivity. This TRD (SW-925) was published by OSW in March 1984 for public comment. It is being revised to incorporate public comments that were received. A draft copy of this document has been sent to ORD where it has been stalled, awaiting clearance. (G.K. Dotson)

Solid Waste Leaching Procedures Manual

This is a report on laboratory batch procedures for extracting or leaching a sample of solid waste so that the composition of the lab leachate is similar to the composition of leachate from waste under field conditions. This TRD (SW-924) was originally published by OSW in March 1984 for public comment and has subsequently been revised with their incorporation. At present, the draft document is completed and awaits clearance by ORD. (C.I. Mashni)

Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals

This TRD summarizes laboratory batch procedures for assessing the capacity of soils to attenuate chemical constituents from solutions such as leachates. It explains the scientific basis and rationale for these procedures and the use of data in designing soil liners for pollutant retention.

It will be issued for public comment in May 1987. Copies will be available for inspection at EPA Libraries in Cincinnati, Washington D.C., Research Triangle Park, and in all ten Regional Offices. It may also be purchased, on paper or microfiche, from the NTIS as PB 87-146155. (M.H. Roulier)

Methods for the Prediction of Leachate Plume Migration and Mixing

This project has developed a variety of computer programs for hand-held calculators, microcomputers, and macrocomputers. The programs predict leachate plume migration from single and multiple sources. The document also contains discussions of sorption, case histories and a field study. A draft for public comment has been postponed until late 1988. (M.H. Roulier)

Hydrologic Evaluation of Landfill Performance (HELP) Model

The HELP Model is a modification of the original waste disposal site hydrologic model entitled, "Hydrologic Simulation on Solid Waste Disposal Sites." This update has incorporated the two-dimensional aspects of landfill cover systems, as well as the addition of the leachate collection system. OSW published this TRD (SW-84-009 and SW-84-010) for public comment in two volumes. These two volumes are available from NTIS (†PB-85-100-840 and †PB-85-100-832, respectively) and include the user's guide for Version 1 and documentation and description of the program. The HELP Model (Version 1) is also available for the IBM PC/XT or compatible computers. Version 2 of the HELP Model is being developed to incorporate public comments and results from verification studies and will be published in late 1987. (D.C. Ammon)

Design, Construction, Maintenance, and Evaluation of Clay Liners for Hazardous Waste Facilities

This 600-page TRD summarizes the state-of-the-art for clay liners as of August 1985. It was issued for public comment in December 1986, is currently being revised, and will be reissued for inspection at EPA libraries in Cincinnati, Washington D.C., Research Triangle Park, and in all ten Regional Offices. The draft TRD may be purchased, on paper or microfiche, through NTIS as PB 86-184496/AS. (M.H. Roulier)

TECHNICAL HANDBOOKS

Eleven technical handbooks have been completed to date. These handbooks cover a variety of techniques on general remedial action guidance, in-place treatment, barriers, decontamination and modeling. A listing of those documents which contain unique state-of-the-art information is shown below, along with a brief description, publication number, and the project officer's name in parentheses.

Review of In-Place Treatment Techniques for Contaminated Surface Soils

This two-volume report presents information on in-place treatment technologies applicable to contaminated soils less than 2 feet in depth. Volume 1 discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2 provides background information and relevant chemical data.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available

from the remedial investigation. Selection of a specific technonlogy involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives.
†PB 85-124881 Vol. 1 (N.P. Barkley)
†PB 85-124889 Vol. 2 (N.P. Barkley)

Handbook for Remedial Action at Waste Disposal Sites (Revised)

The objectives of the Handbook are twofold: (1) to provide the reader with a generalized understanding of the pollutant pathways involved in waste disposal sites, the remedial actions as they apply to each pathway, and the process of selecting the appropriate remedial actions; and (2) to provide detailed information on specific remedial actions including applications, state-of-the-art, design, construction, and/or operating considerations, advantages, disadvantages and cost. EPA/625/6-85/006 (D.E. Sanning)

Handbook for Evaluating Remedial Action Technology Plans

This Remedial Action Technical Resource Document describes how the technologies and methods for evaluating propposed RCRA new hazardous waste disposal sites can be applied to site-specific remedial response activities for uncontrolled hazardous waste sites. The Remedial Action Document is based on the state-ofthe-art technical and cost information in eight TRD's for design and evaluation of new hazardous waste disposal sites under RCRA. That information was reviewed for relevance to remedial response at uncontrolled hazardous waste disposal sites, and then edited to address the needs of personnel involved in response and remedial action planning under CERCLA. †PB 84-118-249 (H.R. Pahren)

Slurry Trench Construction for Pollutant Migration Control

A guidance manual for slurry trench cut-off wall design, construction, and performance evaluation provides recommendations on a variety of scientific and technical parameters relevant to using this approach to isolate hazardous chemicals in near-surface groundwater regimes. The accomplishment of this effort required extensive information gathering and integration of technical data gathered from a diverse array of experience and authorities. †PB 84-177-831 (W.E. Grube)

Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites

A decontamination manual was designed for EPA Program Offices and Regional Superfund Programs as part of the restoration profile of Superfund sites. The manual gives guidelines on 1) the extent to which contamination of buildings, structures and construction equipment can be reduced or eliminated, 2) decontamination methods, 3) economics, 4) health hazards, and 5) availability of equipment/ personnel for the detoxification procedures. Specific waste types found in contaminated buildings, structures and equipment at Superfund sites are identified. Potential secondary impacts of available and potential decontamination treatment methods are addressed in this study. Costs versus risk and projected ultimate site usage are addressed. Methods for monitoring the successfullness of various procedures are defined.
†PB 85-201-234 (N.P. Barkley)

Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites

The objective of this document is to provide technical guidance on the selection and application of models for evaluating remedial action alternatives at uncontrolled hazardous wastes sites. The volumes cover selection of models, simplified methods for subsurface and waste control actions, numerical modeling of surface, subsurface and waste control actions, and analytical and numerical models for evaluation of surface water remedial actions.
†PB 85-211-357 (D.C. Ammon)

Leachate Plume Management

This Handbook summarizes information of leachate plume dynamics and plume management alternatives gained by a study of leachate plume management techniques. Factors that affect leachate plume movement key considerations in delineating the current and future extent of the leachate plume, technologies for controlling the migration of plumes, and criteria for evaluating and selecting plume management alternatives are discussed.
†PB 86-/22330 (N.P. Barkley)

Systems to Accelerate the Stabilization of Waste Deposits

This document investigates in-situ systems which accelerate the stabilization of waste deposits. In-situ applications involve three essential elements: selection of a chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste.

Four reactant categories have been examined: biodegradation, surfactant-assistant flushing, hydrolysis, and oxidation. Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and infiltration beds and galleries. Forced injection (pumping) may also be used. Recovery systems using gravity include open ditching and buried drains, and pumped methods include well-point and deep well systems.
†PB 87-112-306/AS (W.E. Grube)

Covers for Uncontrolled Hazardous Waste Sites

A handbook has been developed which can be used as a guidance document for the selection, design, installation, and long-term maintenance of covers as remedial actions. This handbook provides technical information for regulatory personnel as well as guidance for cover-system designers and construction engineers. †EPA/540/2-85/002 (J.M. Houthoofd)

Stabilization/Solidification of Hazardous Waste

Another handbook has been developed to provide guidance for the evaluation, selection, and use of solidification/stabilization technology as a remedial action alternative at uncontrolled hazardous waste sites. The planning for the application of solidification/stabilization is divided into two phases: process selection and scenario selection. Process selection is concerned with the chemistry of the stabilization/solidification processes in the identification of the composition of the waste. Presented in the handbook are testing and analysis techniques for characterizing waste as a basis for selection of pretreatment and stabilization/solidification processes. Also data are developed on the compatibility of additives and specific classes of waste, and testing systems for the evaluation of stabilizaed/solidified wastes are reviewed. Scenario selection is concerned with the development of equipment requirements, construction sequencing, and cost estimating for the chosen solidification/stabilization process. The handbook presents four basic field scenarios, based on field surveys, that have been used successfully.
†EPA/540/2-86/001 (J.M. Houthoofd)

Fugitive Dust Control at Hazardous Waste Sites

Field studies were performed to determine the effectiveness of dust control technologies at hazardous sites. In the first field study, dust suppressants were tested to determine the effectiveness of fugitive dust control against wind erosion from exposed areas. Based on a tracer sampling protocol, the suppressants were 100 percent effective for 1 to 4 weeks after application, with declining control efficiencies thereafter. The second field study was an evaluation of the effectiveness of windscreens and windscreen/dust suppressant combinations in controlling fugitive dust from storage piles. †EPA/540/2-85/003 (S.C. James)

CONCLUSION

The Technical Resource Documents and the Technical Handbooks that are being prepared and updated by the Land Pollution Control Division (LPCD) are a series of documents which provide best engineering control technolgoy to meet the needs of RCRA and CERCLA, respectively. The TRD's provide design, operation, and evaluation information related to new RCRA hazardous waste disposal facilities to assist the regulated community and the permitting authorities. The Technical Handbooks provide reliable and cost effective remedial action technology information related to Superfund facilities to assist the user community and on-scene coordinators. These documents and handbooks present the sum total of the body of information and experience gained by the Agency over the years on a given topic. As new information is developed, the Agency intends to update each of these documents and handbooks so that they reflect the latest state-of-the-art information.

More information about a specific project or study can be obtained by contacting the project officer referred to in the text. Project Officers can be contacted by writing or telephoning the USEPA, Hazardous Waste Engineering Research Laboratory, Land Pollution Control Division, 26 West St. Clair Street, Cincinnati, Ohio 45268. Phone: (513) 569-7871

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IMPLICATIONS OF CURRENT SOIL LINER PERMEABILITY RESEARCH RESULTS

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ABSTRACT

Since the 1970's hazardous waste legislation has specified soil liner permeability (hydraulic conductivity) as a major criterion for design of soil liners to contain hazardous wastes disposed on land. HWERL studies since 1972 have included over 30 individual projects investigating hydraulic features of compacted soils. Soil/permeant liquid compatibility, applicability of laboratory permeability tests, field permeability testing, effective porosity, and solute transit time have been investigated.

The type of test cell does not appreciably affect the value for permeability measured in the laboratory for water alone. When the permeant liquid contains high concentrations of solutes, rigid wall permeameters show greater increases in permeability (relative to water alone) than triaxial cells. Increasing the hydraulic gradient when using a triaxial cell results in lower permeability values. Triaxial cells and consolidation cells can simulate overburden loading stresses on a soil liner but no data are available to determine how well these laboratory values predict permeability of the soil liner after a landfill cell is completely filled. The compaction mold modified for permeability measurement is the most sensitive geotechnical laboratory method to measure liner/leachate compatibility.

Construction acceptance is being tested with infiltration test devices. Optimum size of infiltration test area versus the number of test sites is being studied. Collection lysimeters installed beneath soil liners offer the most practical means to reliably quantify seepage through the liner system. They also provide an opportunity to collect tracer compounds or leachates solutes for calculation of transit times through the liner.

Examination of soil liners in the field consistently shows heterogeneity in materials, fabric, moisture content, density, and texture. Macrostructural units that provide preferential pathways for rapid flow of liquids are common, but the amount of liquids moving in these pathways is unknown.

Laboratory-measured values demonstrate the lowest permeability that a soil liner material can provide; these values should be regarded as a goal that may be achieved in the field by skilled personnel only under optimum conditions. The uncertainties about permeability/

compatibility testing and the effect of construction practice on permeability of the completed liner dictate that soil liners for hazardous waste facilities must be designed, tested, and built with a much higher degree of care than has been considered routine for civil works.

RATIONALE FOR PERMEABILITY RESEARCH

The Resource Conservation and Recovery Act (RCRA) of 1976 (PL 94-580); as amended in 1984, (HSWA, PL 98-616; and regulations derived from these laws provide that soils can be used as a component of the liner system of a waste disposal facility. EPA regulations specify that the soil liner shall have a permeability of no more than 1 x 10E-07 cm/sec and that the liner shall prevent migration through it during the life of the facility. Specific regulatory requirements are found in the Code of Federal Regulations, 40 CFR Parts 264 and 265, available in public libraries.

Fifteen years ago, questions based on principles of soil chemistry arose suggesting that solvents or other strong chemical compounds in waste and landfill leachates would be expected to attack a soil liner and make it more permeable with time. Results of early research pointed toward several unsolved, related questions:

permeability methodology,
effective porosity,
field-scale measurement,

Since then, EPA's HWERL in Cincinnati conducted over 30 studies evaluating clay soil liner permeability and related issues.

EFFECT OF SOLVENTS AND DILUTIONS ON PERMEABILITY

Our early efforts addressed the question of soil-liner compatibility with leachates (27, 30). Recent articles (2,7,18,30,39) contain the full bibliographies that document work we accomplished determining the value of a permeability test to measure liner/leachate compatibility.

Although much data were generated which demonstrated the adverse effect of pure solvents and high concentrations of other chemical compounds on soil liner permeability, studies using actual landfill leachates of diluted solvents or salt solutions showed an almost undetectable effect in the laboratory studies. A single long-term laboratory study was reported (30) that incorporated actual industrial waste liquids. These results over 10 years show no clear change in soil liner permeability. Recent data (1,6,14) and others continue to demonstrate that in laboratory studies dilute solutions or leachates of only several hundred ppm solutes have no effect.

ASTM methods (mainly D-2434 adapted to low-flow rates) have been applied to determine soil liner permeability (1,2,15,23). Since the early 1980's, other geotechnical engineering testing laboratories and academic civil engineering departments have also conducted numerous experiments investigating various aspects of liner permeability and its measurement. Citations listed (28), document this activity. Johnson and Richter (33) provide an extensive compilation of permeability studies up to 1967. A critical evaluation of all of these published reports is beyond the scope of this paper, but many of the data generated by these studies are important in understanding the current state of soil permeability knowledge.

Extensive data have been reported demonstrating that the permeability of a compacted soil increases as the dielectric constant of the permeant liquid decreases (8,28,36). Although many pure organic liquids have a low dielectric constant, dilute inorganic solutions also possess a low dielectric constant. Neither dilute inorganic solutions nor dilutions of low-dielectric-constant solvents have been shown to significantly affect soil liner permeability. Thus, dielectric constant of a permeant liquid is not per se a meaningful measure of its permeability performance unless it is a pure liquid or a mixture of but a few pure liquids.

PERMEABILITY OF SOIL LINERS CONSTRUCTED IN THE FIELD

Laboratory permeability test results frequently demonstrate that the tested soil presents a hydraulic conductivity less than that of the regulatory threshold, 1 x 10E-07 cm/sec, especially where solute concentrations are in the few hundred ppm range. Recent reports (confirming data first compiled by Olson and Daniel(38), and still widely cited) observe that a liner constructed in the field with the same soil tested in the laboratory has a seepage rate representing a much higher permeability than laboratory test results show. Since the early 1980's our Laboratory has been investigating the reasons for this discrepancy. Thus recent studies have emphasized field performance of hydraulic barriers. Our current research efforts include attempts to (1) quantify the areal variability of soil liner hydraulic properties, (2) obtain an accurate measure of solute transit time through several lifts of liner constructed by field equipment, and (3) determine the feasibility of improving present construction practices in order to obtain a soil liner with a lower overall permeability. These studies are in the early stages and will not be discussed here.

It is clear from numerous laboratory permeability measurements that many soils demonstrate a permeability of 1 x 10E-09 cm/sec or lower. These values can be lowered in many cases by additional measures, such as additives, modified compaction, or other soil handling. Additions of bentonite, lime, Portland cement, and other components to soils in laboratory studies have resulted in substantially lower permeability. Where the hydraulic conductivity is lower than about 1 x 10E-08 cm/sec, diffusion processes move chemical species at the same rate as hydraulic flow. Thus by constructing a relatively thick soil liner, with chemical diffusion governing mobility, pollutants can be prevented from leaving the lined facility through the soil liner for the same or longer time as that provided by a relatively thin liner of synthetic material. Therefore, soil liner thickness of several feet, with attendant permeability of 10E-09 or lower will provide liquid containment at least equal to that obtainable with synthetic materials. The field scale liner must not contain faults at any greater magnitude or frequency than those now found in comparable areas of synthetic materials placed as large sheets. The liner construction industry must demonstrate this at full field scale. The demonstration must include long term containment as measured by lack of seepage through the constructed liner. It will challenge present environmental monitoring techniques to accurately determine that little or no liquids seep through a buried soil structure during a time of many decades.

LABORATORY PERMEABILITY TESTS

Laboratory measurements are made in order to determine whether a candidate soil liner material meets the permeability specification of 1 x 10E-07 cm/sec, or to obtain an evaluation of the compatibility of a soil liner material with a leachate or other solution. The latter purpose is served by noting whether a significant change in permeability occurs when the leachate is introduced into the testing system. Numerous laboratory permeability tests are also being conducted simply to better understand soil/solution interactions.

Soils tested for permeability in the laboratory are first characterized by standard engineering criteria. These normally include

-grain size distribution, including percent fines,

-Atterberg Limits

-water content

-classification by the Unified Soil Classification System.

ASTM procedures for these tests specify that only field-collected soil samples that pass through, at largest, a sieve with 3/4-inch (19mm) openings are to be tested. Indeed, ASTM allows up to 30% of a field sample to contain fragments larger than 3/4-inch before disallowing a Standard Proctor compaction test. It is at this stage--when a soil is specified as being suitable for liner service-- that laboratory testing results exhibit serious shortcomings as predictors of field performance.

Three major apparatuses are used to routinely determine soil hydraulic conductivity in the laboratory: rigid wall cell, or modified compaction mold; triaxial cell modified for permeability testing; and consolidation cell (oedometer) modified for directly measuring permeability. In evaluating the data generated by our studies and those supported by other institutions, it is clear that the differences among permeability values for each of the cell types are not significant when using water and the same soil. This is particularly true if one considers than many commercial geotechnical testing laboratories consider agreement within a factor of two or three to be the best obtainable on replicate permeability analyses of fine-grained soils. A point must be made here that publication of soil liner permeability data in detail greater than two significant figures is probably inappropriate, unless accompanied by detailed description of the laboratory technique.

Permeability testing using a solvent, mixture, or actual landfill leachate presents several problems in a soil permeability test. These are not insurmountable, however. The apparatus degradation problem is solved by using resistant materials, such as stainless steel, plastics, or other substances resistant to chemical attack. In the case of the triaxial cell, several different materials have been used to solve the problem of chemical attack of the confining membrane. Here the user must be certain, however, that some of the stiffer materials used to resist chemical attack, such as Teflon film, aluminum foil, or multiple-layers of these materials, do not interfere with the often-stated advantage of the triaxial method--conforming the Latex membrane to the soil sample surface to remove the possibility of sidewall leakage. If too rigid a membrane is used, the lateral pressure that must be applied so the membrane will conform with the surface of the soil sample may be so high that lateral consolidation occurs.

The potential effect of lateral consolidation must be accounted for in each application of the triaxial apparatus to a study of liner/leachate compatibility. So many data now exist showing that soil permeability decreases with increasing hydraulic gradient--and concurrent increases in lateral confining stress--that the triaxial cell must be discouraged for use in soil-liner/leachate compatibility measurement (31,p.375; 9,pp.72-82; 10,pp.7-8; 35,p.364; 22,p.1654; 45,p.405; 17,Fig.7; 25). We recognize that triaxial confinement is the only practical apparatus to measure the hydraulic conductivity of undisturbed samples of a soil liner, but caution must be urged to apply a confining stress no greater than is present in the field. A few reports in widely distributed technical literature detail the application of the triaxial cell to soil liner permeability testing (10,15,23,29). They commendably present valuable details of the method, but do not adequately emphasize the the need to apply only the lateral stress seen in the field. This restriction effectively prohibits the use of high hydraulic gradients commonly applied to reduce testing time.

The consolidation cell is useful in measuring volume changes of a test specimen during permeation. Applied stress should not exceed field values. Arguments that this apparatus simulates the overburden loading of landfilled waste and that these pressures will heal cracks that may form from leachate interaction with soil liner materials fail to acknowledge the liklihood of variable loading pressures over a liner surface. Placement of drummed waste, for example, may create bridged voids within the landfill, where the liner underneath a drum may experience much higher loading pressure than areas between drums. There are no data available showing the degree of consolidation present in liners beneath land disposal facilities.

The modified compaction mold permeameter described by EPA (43) provides the most immediate information regarding the detrimental effect that a leachate may have on a soil liner material. We recognize that laboratory technicians need to exercise care to ensure that sample preparation within rigid wall cells does not provide immediate sidewall leakage. Soil shrinking because of liner/leachate interaction may rapidly increase measured permeability and cause the testing laboratory to conclude that an incompatibility may exist. The value of the rigid-wall permeability cell in providing a conservative estimate of liner/leachate compatibility, by means of demonstrating a change in permeability outweighs disadvantages such as lack of achieving complete sample saturation. Daniel and Broderick(16) used the compaction mold cell because of its greater sensitivity to potential soil/leachate interactions. Bowders et al.(5) and Daniel et al.(17) discussed the advantages of the rigid and flexible wall hydraulic conductivity cells for studying compatibility. The "double-ring compaction mold permeameter" has been proposed as a device more sensitive to detection of side-wall flow. While this apparatus has desirable features, no published data describing its performance on compacted clay have been found.

Several recent reports relate the results of studies using constant flow rate pumps at high pressure to obtain laboratory permeability results more rapidly (37,12,31). Although data from these investigations provide useful characterization of various soil materials, the sample size of the soil being tested with this technique has been very small. We believe that the larger sample sizes common in commercial geotechnical laboratories reduce data dependence on the careful techniques necessary in these research studies. Testing times of several weeks or months result in long liner/leachate contact times, which improves the credibility of extrapolating laboratory compatibility data to long term field performance. The long testing times necessary to obtain reliable data from the larger sample sizes and modified classical methods have not appeared to present any practical problems to commercial laboratories.

Deciding when stable permeability has been reached and a test can be ended is of greater significance in obtaining a realistic permeability value than the type of laboratory permeability cell. There is lack of agreement within the geotechnical testing community, and we have found that "experience" has dominated the decision-making process. Some laboratories rely upon equal rates of inflow and outflow of permeant liquid to define an equilibrium. Peirce and Witter(39) have recently published a more objective approach to determining whether hydraulic equilibrium has been reached. They point out that frequency of data collection can influence the test termination decision. Cell inflow or effluent volume data can be collected using a variety of buret sizes and collection time points. One should not use calibrated columns of small diameter to increase the accuracy of small flow measurements, but rather base the data collection on porevolume increments that have passed through the soil sample. At this time we suggest 0.05 to 0.10 porevolumes as the smallest increment. We do not know the optimum smallest increment of porevolume of permeant liquid flow that will provide reliable data from which to calculate a permeability value. But, a meaningful and unbiased series of measurements is essential in order to calculate a series of successive permeabilities that may be input to statistical formulas to determine equilibrium. Bryant and Bodocsi (9) also present methods to confirm that an equilibrium permeability has been reached.

FIELD PERMEABILITY TESTS

Demonstrating that a soil liner constructed in the field has the required low permeability is the "proof of the pudding." Field testing of soil liner permeability can be considered from three aspects:

1. Acceptance testing is a measure of the quality of construction in achieving the specified permeability.
2. Performance monitoring provides a measure of the seepage through the soil liner over long periods of use.
3. Transit time is a measure of the time that a soil liner will prevent a leachate solute from migrating out of the bottom

of the liner into the subsoils below a waste disposal facility.

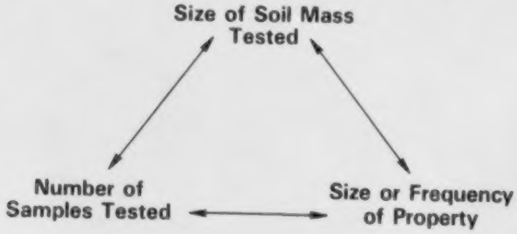

Figure 1. Interrelated problems affecting accurately characterizing the hydraulic performance of a soil liner.

Figure 1 depicts the problems facing us in accurately characterizing the hydraulic performance of a soil liner in-place. This picture does not address methodology problems inherent in trying to quantify very low flow rates characterized by a hydraulic conductivity of 10E-07 cm/sec or lower. Factors such as evaporation loss, liquid flow volume quantification, leak-proof apparatus, determination of when to stop measurements because steady-state flow has been achieved, and statistical treatment of raw data are aspects that must be dealt with.

Numbers of soil samples tested(NSST) to determine the in-the-field permeability is being addressed by geostatistical analyses of data obtained from our studies (41). NSST should be directly related to the size and frequency of occurrence of soil liner discontinutities that provide higher flow rates than allowed by a 10E-07 cm/sec specification. The NSST are likely to be severely affected by economic considerations and by the need to protect the environment from landfill seepage. The size of the soil mass tested refers to the diameter of a core or to the surface area of the sample being examined. The sample needs to be sufficiently large to include representative soil properties, both well-mixed homogeneous mass as well as occasional regions of heterogeneities that permit higher hydraulic flows.

The property of the soil liner being tested is the hydraulic flow rate. As discussed later in this paper, flow appears to be dominantly controlled by porous regions in a heterogeneous soil liner. The spatial extent of these discontinuties in the liner matrix needs to be known so that they can be accounted for in sampling schemes. You need to know the size and distribution of hydraulic discontinuities in order to reliably detect hydraulic discontinuities. In practice the trade-offs depicted in Figure 1 need to be recognized and accounted for in sampling schemes.

EPA's Minimum Technology Guidance(44) states a purpose of the compacted soil liner is to decrease leakage in the event of leakage through the FML component, and increase the efficiency of the secondary leachate collection system. In order to be effective for this purpose, the compacted soil liner must be uniform in its property of low permeability. Field permeability tests must be aimed toward evaluating the permeability uniformity of as large soil liner masses as possible. Determination that a soil liner meets a hydraulic conductivity specification must therefore take into account the area of liner tested, as well as the validity of the measurement method. If one suspects that a certain proportion of the soil liner contains flaws that will permit high seepage rates, then these flaws should be included within the area of soil liner evaluated to ascertain whether the permeability specification has been met. In this case either a large area should be evaluated for permeability, or adequate areal representation by numerous small samples must be provided and should be consistent with accepted statistical practice. The questions of how many samples, and of what size, must be addressed. We believe that large area infiltration and seepage data obtained from a test section constructed with full scale equipment represents the current state-of-the-art.

Construction Acceptance Testing

In reports of soil liner design and construction it is often stated that the lowest permeability is obtained by compacting at a moisture content wetter than the optimum found on a moisture-density curve after Proctor compaction. Recent laboratory studies(30, 9, 4,) reinforce the data from early studies by Lambe and Mitchell showing lower hydraulic conductivity as the soil is compacted at moisture contents wet of optimum. It is unclear exactly at what moisture content wet of optimum the field workability of a clayey soil becomes impossible. Our experience is that construction contractors tend to be quite conservative--in that they will err on the dry side because they know that soil that is extremely wet is more difficult to compact.

Figure 2 shows the variation in compaction moisture content across an intensively studied soil liner section of 1/20 acre. In this case the optimum moisture was 17.8%; 95% and 105% of optimum are 16.9% and 18.7% respectively. We have collected both infiltration and seepage data from this soil liner area and have calculated comparable permeabilities. We are currently measuring the permeabilities of intact cores taken from an intensive sampling array across this experimental area. These data will comprise an extensive set comparing laboratory and field permeability under carefully controlled conditions.

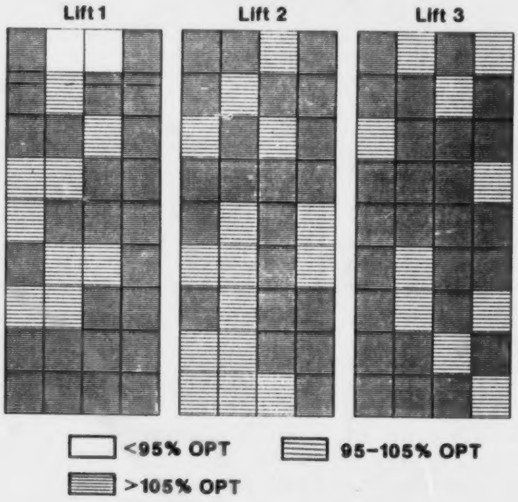

Figure 2. Distribution of compaction moisture contents in 3 lifts of an experimental soil liner based on nuclear surface moisture meter (from 41).

Large infiltration rings, particularly the recently developed closed inner ring types, are being rapidly accepted by state and private organizations. Using large rings appears to be the best current approach to more rapidly verify the quality of soil liner construction. Steady state flow has been achieved after only a few days (19). Objections have been voiced that these devices only evaluate the surface few inches of a total liner installation. Known applications so far have been on soil liner test sections, completed facility liners, and clay cover soil layers. They can also be used to test different lifts in a liner section several feet thick. Infiltration ring approaches simulate an event where a small pond of leachate comes into contact with a soil liner, such as leakage from above. Large closed-top infiltration rings are easy to install and monitor and can represent a significantly large area. Small double-ring apparatuses, such as applied to "perc-tests" for wastewater application to agricultural fields, should not be used for soil liner testing unless extensively modified. Evaporation control and accurate measurement of small flows are essential in determining field permeability. Several in-situ permeability test methods have been recently described (20); it was concluded that an objective of an in-situ test should be to evaluate a representative volume of soil. Clearly, this objective can be better met by using larger devices.

Our observations of dye infiltration from water ponded on test sections and our morphologic examination of soil fabric lead us to conclude that soil liner test sections must be constructed in at least four lifts. We have observed large variability in amounts of unbroken native soil clods in the first lift above the liner foundation and variable thickness in the surficial lift where the surface has been bladed to reach a specified grade. Reades (40) also appears to negate the value of the surface lift. If one constructs a test section of only four lifts, potential construction compromises that are present in the basal and surficial lifts leave only the middle two lifts as the effective hydraulic barrier. Thus a fault, such as inter-lift transport paths between the two middle lifts, brings about high permeability results and/or short solute transit times through the total test section. The design, construction, and operation of a field-scale permeability test on the test section of a soil liner has evolved into a much greater task than the usual compaction test section practiced by all earthwork engineers. Further, present construction quality assurance guidelines require documentation that the entire facility liner was constructed in the same manner as was the test section, so that test section data are accurately representative of the full-scale soil liner performance.

The presence of heterogeneity in the soil mass of the test section requires that the factors depicted in Figure 1 be applied to permeability and other tests applied to the test section. Cores taken for laboratory analyses or installation of small diameter in-situ permeability sensors may evaluate too small a volume of soil to capture major hydraulic pathways. Thorough soil pulverization or mixing may reduce these problems.

The nuclear surface moisture-density meter, in backscatter mode, is routinely used to verify that the design specifications are met on a compacted soil liner. Figure 3 clearly shows that the detected neutron backscatter is reflected by the total soil mass in perhaps a 9-inch cube beneath the instrument. Our observations of permeant liquid flow along fracture planes, faces of adjoining unbroken native soil clods, and small-scale less dense regions where compactor feet have not directly compacted the soil suggest that the soil volume exposed to the area and volume averaging effect of the neutron probe is simply too large for the neutron probe to detect significant liquid flow pathways. Where research data have consistently shown that only a small percentage of the liner mass is active in permeant liquid transmission, it follows that a measurement of bulk properties of a soil liner is unlikely to detect small flaws that are hydraulically significant. This conclusion simply means that the industry would benefit from a construction quality measurement technique that can reliably detect small soil liner discontinuities .

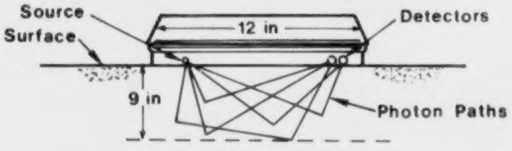

Figure 3. Geometry and scale considerations of nuclear moisture-density probe in backscatter mode (from 42).

Long-Term Performance

The Hazardous and Solid Waste Amendments of 1984, and ensuing regulations, specify that no constituent shall migrate through a lower soil liner "...during the period such facility remains in operation (including any post-closure monitoring period)." This period normally is several decades. A recent article (11) referred to a Canadian study that found that numerous hazardous waste disposal sites "leaked after an average of 14 years." Long-term containment performance of a soil liner can only be measured by detecting leakage, or its absence. Collection lysimeters appear to be the most credible means to measure the quantity and quality of liquid that seeps through a soil liner over an extended time period(Fig. 4). Some type of underdrain system is also needed to collect seepage that can be analyzed to evaluate the transit time of solutes through a soil liner. The State of Wisconsin has for several years been requiring the installation of collection lysimeters beneath lined disposal facilities (34). Clearly, a device that intercepts and quantifies leachate exiting at the bottom of a liner is the best means of determining whether and when a constituent has passed through the liner. The collection lysimeter, however, is not a simple answer to satisfying the regulations. Sizes of the leachate interception area in a compilation (34) of Wisconsin lysimeters ranged from 25 sq ft to 7,400 sq ft. The installation of these collection lysimeters must be made very carefully to ensure that any and all liquids collected are not lost but are conveyed to an outlet for measurement (or treatment if in significant quantities). Long-term performance measurement requires that a collection lysimeter be placed beneath the entire volume of the liner and not arbitrarily located in some convenient area of the surface or other region of the liner. Design, materials, and construction must incorporate the highest possible quality for two important reasons: (1) the collection structure must perform perfectly for an unknown long time period, and (2) after construction, the lysimeter will be unseen and unaccessible for any future maintenance. Alternative long-term performance monitoring schemes, such as monitoring well arrays are not within the scope of this paper.

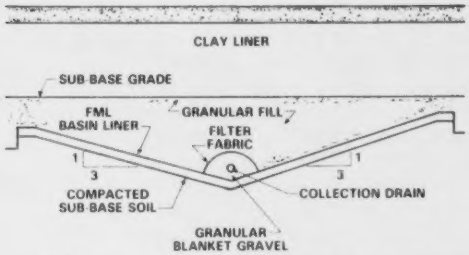

Figure 4. Cross section of a leachate collection lysimeter.

Transit Time

To gain approval, an applicant for a land disposal facility construction permit normally provides hydraulic conductivity data on the soil to be used in a liner. "Knowledge of the liner permeability is not sufficient information to accurately estimate the length of time of liner effectiveness" (32). To demonstrate that leachate constituents will not pass through a proposed liner system, a test section of compacted soil liner is an accepted structure to demonstrate hydraulic performance. Installing a collection lysimeter beneath this test section provides an opportunity to collect any seepage passing through if water or other liquid is ponded on the surface. Figure 5 depicts a possible approach to such a test section. Adding tracer compounds to surface ponding allows ready observation of whether and when a solute exits the bottom of the liner. We find very few published data indicating liquid or solute transit time for soil liners built in recent years. One company has installed detection electrodes to try to monitor passage of a wetting front through a soil liner.(3)

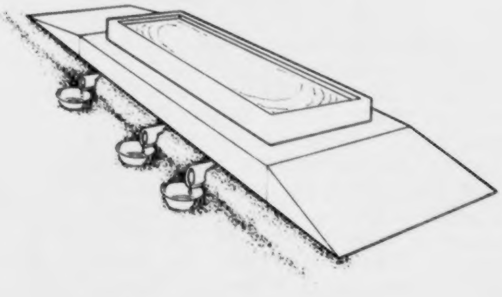

Figure 5. Ponded or underdrained test fill.

Our experimental studies show a rapid transit time of tracer solutes through several lifts of compacted soil; these soil liners demonstrated low permeabilities, less than 1 x 10E-07 cm/sec. Careful examination of the compacted soil lifts involved have clearly shown that dyed liquids follow a few preferential pathways through a lift: commonly moving laterally across a lift interface and thence again downward through a small zone in the next lift. Footed compaction rollers are widely used to achieve the shear deformation of a kneading process shown by laboratory studies to result in lower permeability than static or impact compaction.

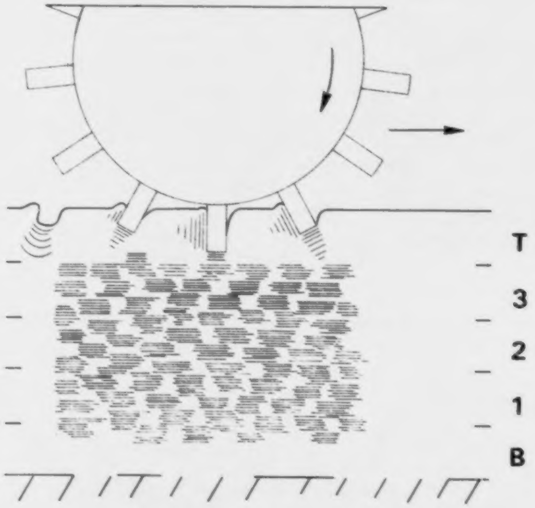

Figure 6. Compaction of a multi-lift soil liner by a footed roller.

Figure 6 illustrates the variability in compaction produced by a footed roller where the number of passes has been inadequate to completely cover the surface of the lift being compacted. Although the number of passes must depend on the foot area and the roller drum's foot density, at least 18 passes must be made with commonly available footed rollers to completely compact an area. Our observations of vertical cross-sections of soil liners several feet thick show amazing heterogeneity within a compacted lift and adjacent lifts. We conclude from liner profile studies that regions of lesser density, even as small as a centimeter in dimension, comprise a significant fluid flow pathway.

Our observations are consistent with the critical view of liner macrostructure by Folkes (24). A percolating liquid seeks the path of least resistance, which need not be a clear desiccation crack or fracture within a liner of otherwise plastic soil. These observations support hypotheses that lack of uniform soil compaction is a major contributor to high seepage rates through soil liners. Figure 7 compares the constructed fabric of a compacted soil where it must support a load and where it must contain a liquid. We believe that structural competence has not yet been shown to provide the liquid containment required of a landfill liner.

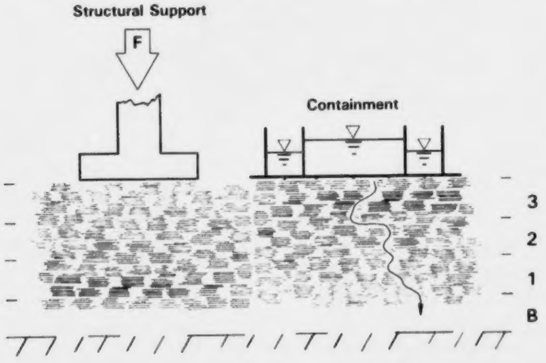

Figure 7. Multi-lift soil compacted by footed roller and used for support or containment.

Where cracks and/or less-dense soil regions are connected, a ponded liquid will penetrate the liner system much more rapidly than transit time models predict. We have only been able to characterize these flow pathways in field-constructed liners using dyes in ponded water, followed by careful soil morphology studies of excavated liners cross-sections. Liner morphology studies have also illustrated the dramatic effect of unbroken native soil clods in providing liquid flow short-circuits. Daniel's laboratory study of chunk size vs permeability (13) has been widely cited as illustrative of the effect of soil clod size on permeability. Folkes (24) brought out the dependence of compacted soil permeability on soil structure, aggregate orientation, and other factors. He also cited several earlier studies that concluded that permeability is controlled by macropore distribution. Dunn (21) has recognized the importance of the structure of the field-compacted soil liner in restricting fluid flow. The chunk-size in Daniel's study--1/16 to 3/8 inch--represents laboratory sieving, and field liner soils are unlikely to be limited to uniform clods this small. Field-run borrow soils commonly contain gravel-sized stones or soil clods, unless carefully screened. In examining field-constructed soil liners, we invariably see evidence of fluid flow around the surfaces of gravel or soil clods retaining their native size. We also see evidence that these native gravel or clods are pushed intact through the matrix of surrounding soil during lift compaction. Frequently a relatively smooth plane results where a gravel or clod has been so pushed. Close examination has clearly shown these planes to be paths of liquid flow. Failure to break down clods of native soil during liner construction creates the mechanism for rapid transit time through the soil liner simply by increasing the heterogeneity of the liner.

Laboratory studies of liquid or solute transit time have tried to identify a more accurate measure of "effective porosity " of soil liners. Effective porosity has been described as that portion of the total liner porosity that contributes significantly to fluid flow. We have conducted several investigations showing that effective porosity determined on laboratory prepared compacted clay soils and in limited field investigations is only in the range of a few percent (32). That is, effective porosity comprises only about 10% of the total liner porosity. Gordon (26) presents a model for effective porosity where fracture characterization and continutiy are known. It requires input of field data for fractures, but continuing porous zones could probably be handled as well.

Collection lysimeters, porous probes placed at different depths, or relatively unverified technologies of wetting front detectors represent the range of methods available to quantify leachate transit time. Computer model predictions of transit time have thus far been unable to accurately predict field events. This is because soil liners constructed in the field contain properties and features which have been excluded from models.

CONCLUSIONS

Laboratory-measured liner soil permeabilities demonstrate the lowest values that a soil material can provide; these values should be regarded only as a goal that may be achieved in a field structure by skilled personnel under the best conditions.

Use of the modified compaction mold for liner/leachate compatibility tests removes an unaccounted-for variable in consolidation cells and triaxial cells. This variable is the applied stress that is likely to close actual desiccation cracks or densify small porous zones. Although substantial stresses are present on soil liners in place underneath waste fills, it is likely that this will not be uniform, and unstressed or weakly stressed regions may allow permeation of leachates.

A substantial data base exists demonstrating the adverse effect of pure or relatively pure organic solvents on compacted soil liners. Long-term effects of soil liner exposure to dilute chemicals or leachates have not yet been demonstrated. Available data have resulted in regulations that now prohibit land disposal of solvents or free liquids.

Traditional soil moisture-density measurement procedures are unlikely to detect soil liner features that are hydraulically important.

Innocuous tracer compounds, such as dyes and inorganic ions, when added to water ponded on liner test sections can be detected in pore water or seepage water. Collection lysimeters or porous probes within the soil liner can be monitored for the presence of tracers. Time of detection after addition can be used to calculate realistic solute transit times through the soil liner.

Collection lysimeters must be installed under liner areas that are representative of the total liner area. The underdrained area must not be constructed with special care that is not applied to the rest of the facility liner. Long-term soil liner performance can only be determined by long-term monitoring.

The references cited in this paper should be examined, but also the references in the cited papers should be studied because they provide essential background.

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THE BEHAVIOR AND ASSIMILATION OF ORGANIC AND INORGANIC PRIORITY POLLUTANTS CODISPOSED WITH MUNICIPAL REFUSE - A PROGRESS REPORT

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ABSTRACT

The behavior and possible assimilation of organic and inorganic priority pollutants codisposed with refuse are being investigated in ten simulated landfill columns operated under single pass leaching or leachate recycle. The priority pollutants include selected organic compounds and three different loading levels of heavy metals mixed with municipal refuse. After being brought to indicated field capacity with water additions, leachate and gas from the ten columns were analyzed for routine indicator parameters as well as the selected priority pollutants.

Preliminary results indicate that the presence of priority pollutants exhibited little apparent influence on the progress of refuse conversion into the acid fermentation phase of stabilization. Trends indicative of assimilative capacity, particularly with respect to the inorganic priority pollutants, are beginning to be established as the various biological and physical-chemical mechanisms of attenuation take effect. Microbial mediation of the chemical environment has encouraged precipitation and complexation or sorption of admixed species as gas and leachate constituents are partitioned and released from the waste mass. Moreover, leachate recycle tends to regulate this process, contain the various leached ingredients in a more homogeneous medium, provide greater saturation and contact opportunity, and permit better inspection and operational control of the overall mechanisms of *in situ* assimilation.

INTRODUCTION

Landfill codisposal of municipal refuse and organic and inorganic priority pollutants emanating from households and small quantity hazardous waste generators has become common practice in many areas throughout the country. Unfortunately, this practice has received limited scientific scrutiny and a general lack of understanding prevails with respect to loading limits and associated potentials for adverse environmental impact. Therefore, comprehensive evaluation of these impacts and the possibility for assimilation of hazardous wastes at such landfill disposal sites is being addressed by simulated codisposal investigations at the Georgia Institute of Technology.

The information presented and discussed herein is a summary of research progress into the mechanisms controlling and defining loading capacities and impacts on the *in situ* processes of waste stabilization when influenced by single pass leaching or leachate recycle in landfills. Therefore, comprehensive gas and leachate analyses have been scheduled over a three-year project period. From these analyses, early results on the variations in leachate mercury and lead, as well as measurable organic priority pollutants, are used to typify stabilization trends and reveal the complexity of the landfill environment and its inherent ability to accommodate and attenuate toxic loadings.

MATERIALS AND METHODS

Column Design and Operation

The ten simulated landfill columns were designed in pairs with the operational features illustrated in Figure 1. Each column was constructed of two 0.9-m diameter steel sections, with a total height of 3.0 m. Five of the columns were designed to operate with single pass leaching, whereas the other five were designed to facilitate leachate collection and recycle. All columns were provided with appropriate appurtenances and were sealed gas-tight after loading.

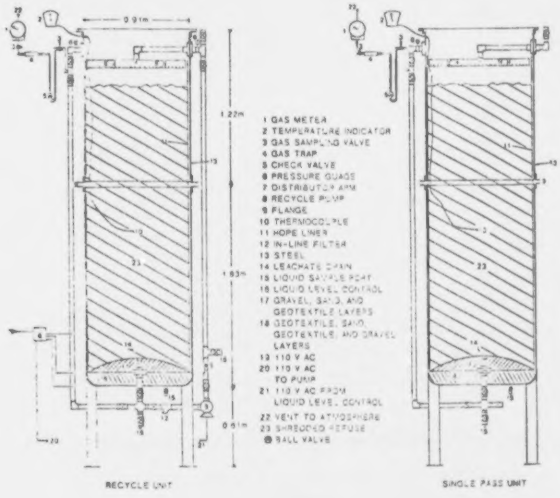
0.91m
1.22m
1.83m
0.61m
1 GAS METER
2 TEMPERATURE INDICATOR
3 GAS SAMPLING VALVE
4 GAS TRAP
5 CHECK VALVE
6 PRESSURE GUAGE
7 DISTRIBUTOR ARM
8 RECYCLE PUMP
9 FLANGE
10 THERMOCOUPLE
11 HDPE LINER
12 IN-LINE FILTER
13 STEEL
14 LEACHATE DRAIN
15 LIQUID SAMPLE PORT
16 LIQUID LEVEL CONTROL
17 GRAVEL, SAND, AND GEOTEXTILE LAYERS
18 GEOTEXTILE, SAND, GEOTEXTILE, AND GRAVEL LAYERS
19 110 V AC
20 110 V AC TO PUMP
21 110 V AC FROM LIQUID LEVEL CONTROL
22 VENT TO ATMOSPHERE
23 SHREDDED REFUSE
BALL VALVE
RECYCLE UNIT
SINGLE PASS UNIT

Figure 1. Simulated landfill columns.

The pair of single pass and recycle control columns were loaded with shredded municipal refuse only, whereas the remaining four pairs of test columns were loaded with selected organic priority pollutants codisposed with shredded municipal refuse. Three pairs of these latter test columns also received incremental loadings of toxic heavy metals in the form of alkaline metal finishing waste treatment sludge spiked with additional heavy metals. The loading levels for the simulated landfill columns are indicated in Table 1.

After loading and sealing had been completed, tap water was added to bring each column to indicated field capacity and initiate the immediate production of leachate for recycle and/or analysis. Thereafter, water was added at a rate of six liters per week for the single pass columns and similarly to the recycle columns until sufficient leachate had accumulated to accommodate recycle and analysis schedules.

Leachate and Gas Analysis

Once leachate was generated from each of the ten columns, a comprehensive analytical program was established for the common indicator parameters as indicated in Table 2. For the purposes of this

TABLE 2. LEACHATE AND GAS MONITORING PARAMETERS AND METHODS

Measurement	Reference	Precision Std. Dev.	Accuracy
Conductivity	EPA 600/4-79-020 Method 120.1	±6%	95-105%
pH	EPA 600/4-79-020 Method 150.1	±0.1 SU	±0.1 SU
Alkalinity	EPA 600/4-79-020 Method 310.1	±5%	95-105%
Cl^-, SO_4^{-2}, PO_4^{-3}, S^{-2}	Standard Methods Method 429	±10%	90-110%
NH_3-N	EPA 600/4-79-020 Method 350.3	±5%	90-110%
ORP	ASTM Method 1498-99	-	-
BOD_5	EPA 600/4-79-020 Method 405.1	±20%	-
COD	EPA 600/4-79-020 Method 410.1	±10%	90-110%
TOC	EPA 600/4-79-020 Method 415.1	±10%	90-110%
$CH_4/CO_2/H_2$	Gas Chromatography	±5%	90-110%
Cadmium	EPA 600/4-79-020 Methods 213.1 & 213.2	±10%	90-110%
Calcium	EPA 600/4-79-020 Method 215.1	±5%	90-110%
Chromium	EPA 600/4-79-020 Methods 218.1 & 218.2	±10%	90-110%
Iron	EPA 600/4-79-020 Method 236.1	±10%	90-110%
Lead	EPA 600/4-79-020 Methods 239.1 & 239.2	±10%	90-110%
Magnesium	EPA 600/4-79-020 Method 242.1	±5%	90-110%
Manganese	EPA 600/4-79-020 Methods 243.1 & 243.2	±10%	90-110%
Mercury	EPA 600/4-79-020 Method 245.1	±20%	80-120%
Nickel	EPA 600/4-79-020 Methods 249.1 & 249.2	±10%	90-110%
Potassium	EPA 600/4-79-020 Method 258.1	±5%	90-110%
Sodium	EPA 600/4-79-020 Method 273.1	±5%	90-110%
Zinc	EPA 600/4-79-020 Methods 289.1 & 289.2	±10%	90-110%
Lithium	Standard Methods Method 317B	±5%	95-105%
Solid Waste Calorific Value	Parr Instruments Tech. Manual #130	-	-
Solid Waste Moisture	Ohaus Instruments Tech. Manual	±5%	90-110%
Volatile Organic Acids	Direct Aqueous Injection Capillary Column G.C.	±10%	90-110%

TABLE 1. LOADING LEVELS FOR SIMULATED LANDFILL COLUMNS

Loading	Column Identity*									
	1(CR)	2(C)	3(O)	4(OL)	5(OM)	6(OR)	7(OLR)	8(OH)	9(OMR)	10(OHR)
Shredded Municipal Refuse, kg (dry)	267	267	267	267	267	267	267	267	267	267
Priority Organic Pollutants, g										
Dioctyl phthalate	-	-	120	120	120	120	120	120	120	120
1,2,4-Trichlorobenzene	-	-	120	120	120	120	120	120	120	120
Dibromomethane	-	-	120	120	120	120	120	120	120	120
Lindane	-	-	120	120	120	120	120	120	120	120
Hexachlorobenzene	-	-	120	120	120	120	120	120	120	120
2,4-Dichlorophenol	-	-	120	120	120	120	120	120	120	120
2-Nitrophenol	-	-	120	120	120	120	120	120	120	120
1,4-Dichlorobenzene	-	-	120	120	120	120	120	120	120	120
Naphthalene	-	-	120	120	120	120	120	120	120	120
Dieldrin	-	-	30	30	30	30	30	30	30	30
Nitrobenzene	-	-	120	120	120	120	120	120	120	120
Trichloroethene	-	-	120	120	120	120	120	120	120	120
Priority Inorganic Pollutants, g										
Cadmium	-	-	-	26.1	52.3	-	26.1	104.6	52.3	104.6
Chromium	-	-	-	45.3	90.6	-	45.3	181.2	90.6	181.2
Mercury	-	-	-	20.3	40.6	-	20.3	81.2	40.6	81.2
Nickel	-	-	-	39.7	79.4	-	39.7	158.8	79.4	158.8
Lead	-	-	-	104.9	209.8	-	104.9	419.6	209.8	419.6
Zinc	-	-	-	45.7	91.4	-	45.7	182.8	91.4	182.8

*Letters in parentheses indicate control (C) or recycle (R) columns; organic (O) loadings; and, low (L), moderate (M) or high (H) inorganic loadings.

presentation, the protocols established for the determination of leachate heavy metals, selected anions, ORP, pH and conductivity were of particular interest with the latter analysis being used to estimate the influence of ionic strength and activity on solubility or complexation equilibria.

In the case of the selected organic priority pollutants, leachate samples were spiked with surrogate compounds and extracted for four hours with methylene chloride using a continuous vapor phase procedure. After drying over anhydrous sodium sulfate and concentration to a volume of 1.0 to 4.0 mL in a Kuderna-Danish apparatus, the samples were analyzed by capillary column gas chromatography-mass spectrometry (GC-MS) using an internal standard. Results were validated by a number of quality assurance quality control (QA/QC) procedures, including analysis of duplicate samples, spiked samples and blanks. In addition, calibration curves were developed for each set of samples using serial dilutions of standard solutions.

For those organic compounds capable of being transferred by volatilization or stripping to the gas phase, gas traps containing 2 to 2.5 g of Tenax adsorbent resin were inserted into the gas collection systems of each simulated landfill column. These traps were removed periodically and the organics desorbed by heating at 150°C for two to four minutes. The desorbed organic compounds were transferred directly to a capillary column and measured by GC-MS.

RESULTS AND DISCUSSION

As indicated previously, this presentation will focus on the behavior and fate of selected priority pollutants as the landfill columns progressed through the initial phases of landfill stabilization. Accordingly, as has been described in detail elsewhere (1), current operation of the columns has been intentionally maintained in the acid formation phase, as indicated by the low pH and high chemical oxygen demand (COD) and total volatile acids (TVA) concentrations illustrated in Figure 2. This operational condition is necessary to assess the effects and implications of the test loadings during a period when the leachate is most aggressive and mobility generally most enhanced.

Changes in Selected Heavy Metals

Based upon a fundamental understanding of the reactivity of the various heavy metals within the landfill environment (2), mercury (Hg) and lead (Pb) were selected as a focus for this presentation. Accordingly, the two most significant inorganic anions capable of affecting the mobility of these metals were sulfate ($SO_4^=$) and chloride (Cl^-). As indicated in Figures 3 and 4, their disposition in the leachate from the single pass columns with time indicated a typical washout pattern analogous to a conservative tracer. However, the concentrations in the leachate from the recycle columns, rather than indicating an essentially constant level to be expected with a conservative

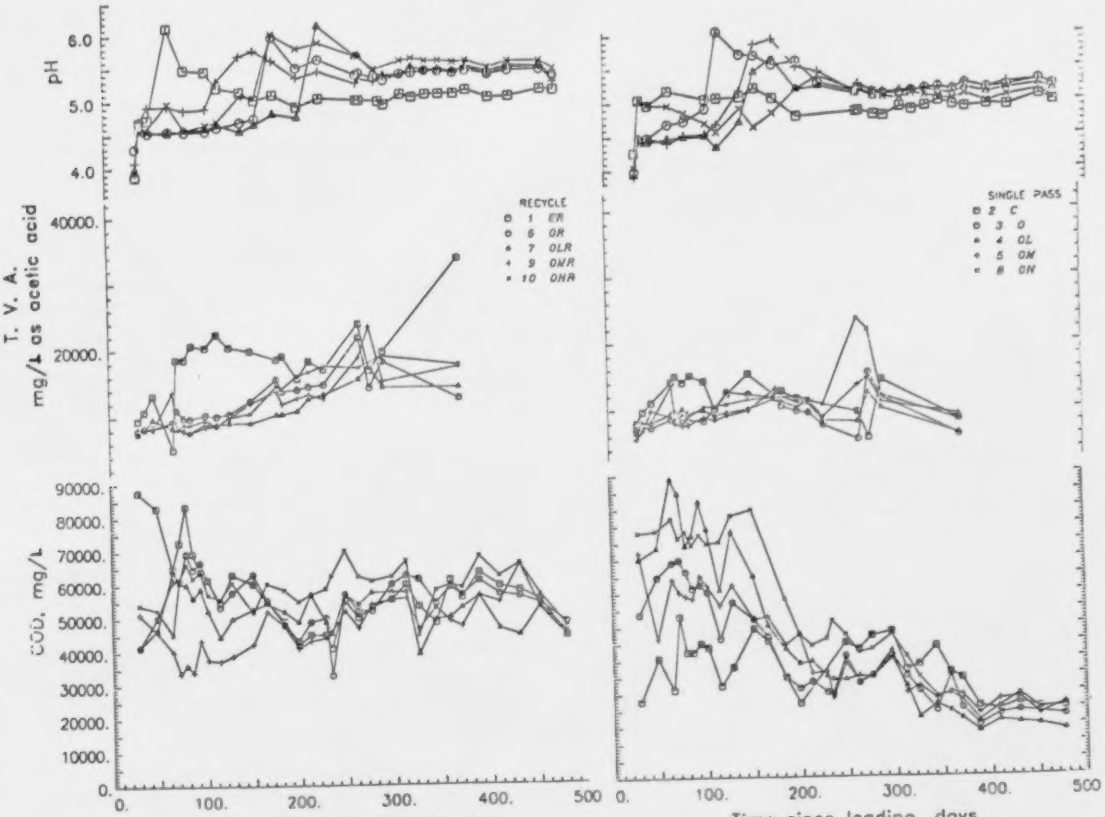

Figure 2. Leachate COD, TVA and pH for recycle and single pass landfill columns.

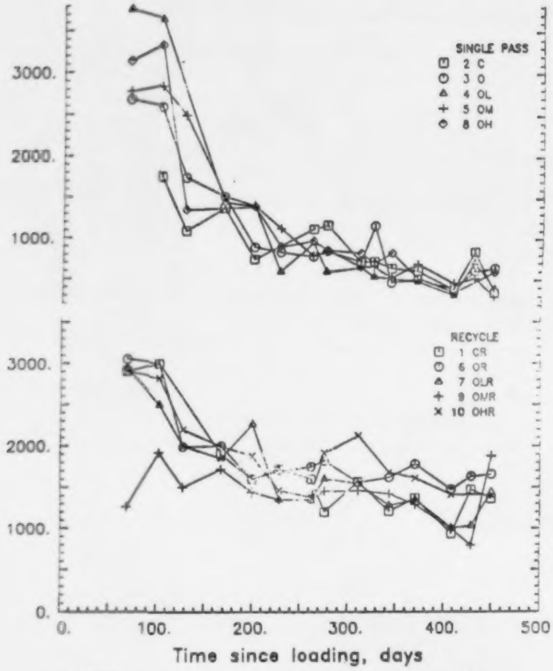

Figure 3. Leachate sulfate concentrations for recycle and single pass landfill columns.

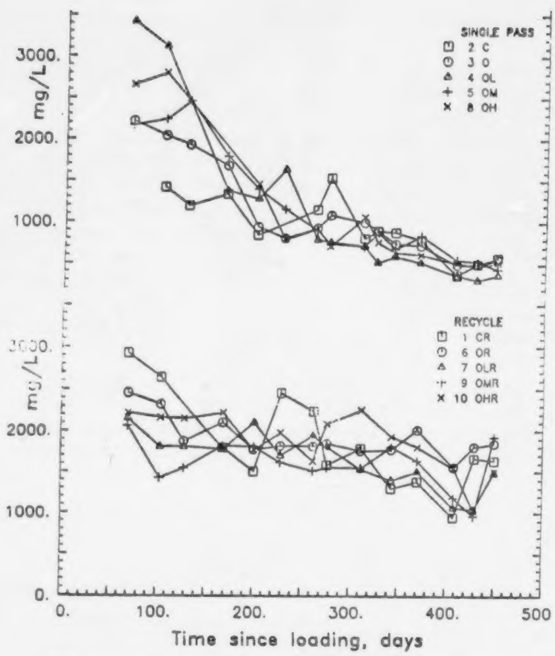

Figure 4. Leachate chloride concentrations for recycle and single pass landfill columns.

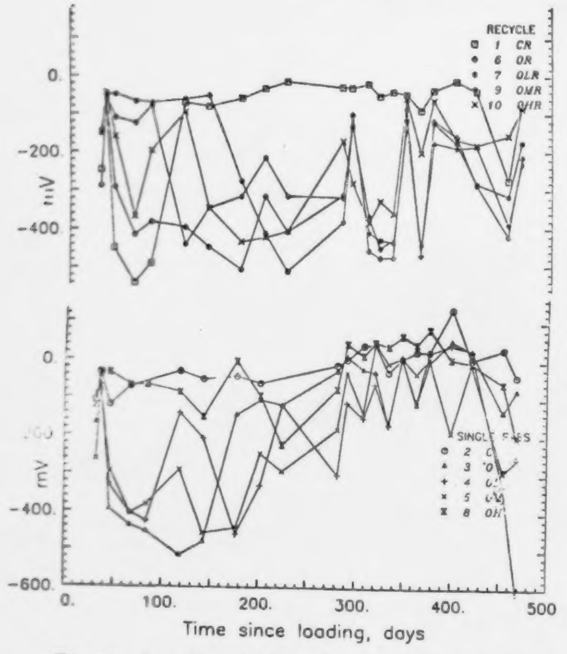

Figure 5. Leachate ORP for recycle and single pass landfill columns.

tracer, also decreased with time. In searching for a cause for such a decrease, possible mechanisms influencing removal of Pb and Hg included complexation and precipitation and reduction of sulfate to sulfide under the anaerobic conditions prevailing within each landfill column.

As indicated in Figure 5, the likelihood of reduction of sulfates to sulfides was reinforced by the presence of reducing conditions characterized by negative redox potentials (ORP). Since sulfides serve as potent precipitating agents for most heavy metals, their presence in even very low levels will control metal solubilities. Moreover, ORP is significant in determining the chemical state of heavy metals, their potential for reaction and their ultimate mobility.

The perturbations in the figure indicate that ORP is a procedure and condition sensitive analysis which frequently measures only trends rather than absolute potentials. It is affected by the medium within which the measurement is made and by external influences during sampling and analysis. Exposure to air, contamination of electrode surfaces, and non-homogeneous mixing all tend to hinder absolute measurements and often cause irregularities in determination. Nevertheless, the consistently negative ORP values were sufficiently indicative of reducing conditions to allow the presumptive diagnosis that follows.

Similar difficulties were encountered with the absolute measurement of sulfide due to fouling of the electrode surface. Moreover, during this period of investigation, sulfide levels were often below detectable concentrations and were also influenced by reaction with the heavy metals.

In terms of the two heavy metals chosen for discussion here, mercury solubility and speciation can be subject to a complex array of factors including reduction, precipitation and complexation. Although the mercury was added in the form of mercuric compounds, reduction to mercurous ion or to metallic mercury could occur under conditions of relatively low ORP. Moreover, unlike the other heavy metals loaded into the columns mercury shares with lead the propensity to form sparingly soluble chlorides, sulfides and sulfates. Sulfide forms very sparingly soluble precipitants with both mercuric and mercurous ions and can control mercury solubility even if present in below detectable levels. Likewise, mercuric ion is subject to moderately strong complexation by chloride and, in the presence of existing leachate chloride levels (Figure 4), the neutral complex, $HgCl_2$, would be the overwhelmingly dominant soluble species of divalent mercury.

To inspect the behavior of mercury as landfill stabilization progressed with time, leachate mercury concentrations have been plotted in Figures 6 and 7 on both normal and expanded scales, respectively. The expanded scale plot was necessary to

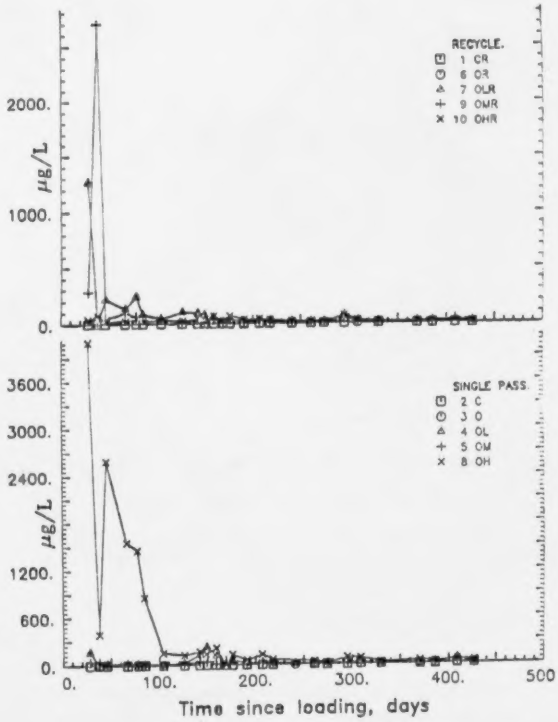

Figure 6. Leachate Hg concentrations for recycle and single pass landfill columns.

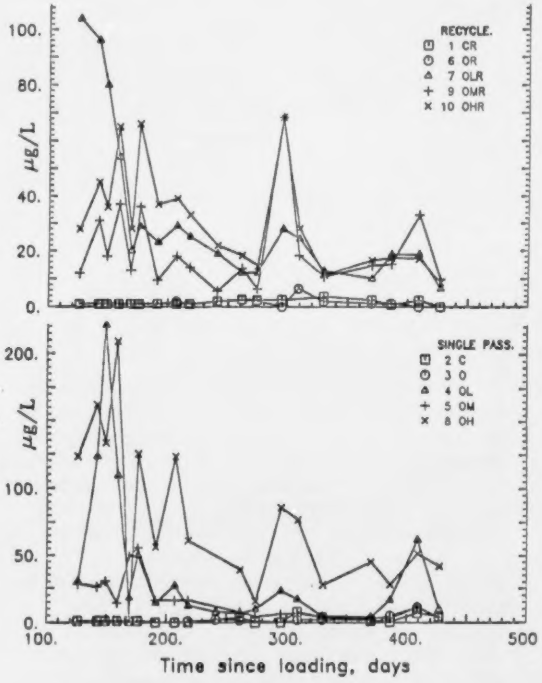

Figure 7. Leachate Hg concentrations for recycle and single pass landfill columns (expanded scale).

compare the dissolved mercury levels when leachate mercury concentrations had become very low. Examination of these figures indicates that, following the initial elevated levels of leachate mercury for the six spiked columns, the concentration decreased rapidly to levels generally below 50 µg/L.

To help explain this behavior, a pC-pE diagram for the $Hg^{+2}/HgCl_2/Hg^\circ$ system at pH 5.2 is presented in Figure 8. The component equilibria suggest that, at the negative redox potentials and acid pH conditions prevailing in the landfill columns, the mercuric compounds added will be reduced to metallic mercury. This finding is consistent with other reports of metallic mercury in water at concentrations of 20 to 40 µg/L (3,4), and is of major significance in determining eventual fate, including the possibility of volatilization, particularly when methane fermentation with gas stripping prevails.

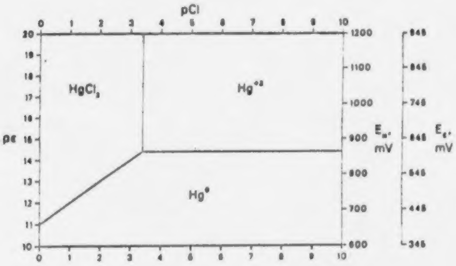

Figure 8. pC-pE diagram for $Hg^{+2}/HgCl_2/Hg^\circ$ system at pH 5.2.

Lead, the other heavy metal selected for analysis here, contrasts with mercury in that it will be expected to remain in the divalent state under current operating conditions. This state subjects lead to two significant reactions which control its solubility. First, lead is susceptible to precipitation as sulfide, sulfate or chloride. Secondly, while not as prone to form very strong complexes as the ionized forms of mercury, lead will form such complexes with sulfate and chloride and will thereby tend to increase lead solubility beyond that otherwise predicted by simple dissolution. Moreover, if there is a preference for reduction to metallic mercury, then in the absence of mercury ions, lead will preferentially react with sulfide over the other heavy metals loaded into the columns.

To associate these concepts with an interpretation of changes in leachate lead concentrations, Figure 9 indicates that initial high lead levels decreased rapidly and then tended to increase again, particularly in the most heavily loaded columns. A possible explanation of these changes could be predicated on two considerations. First, sulfide, even at very low concentrations, would be the primary precipitant for lead. Secondly, if sulfide is absent, either sulfate or chloride will function as the reacting anions.

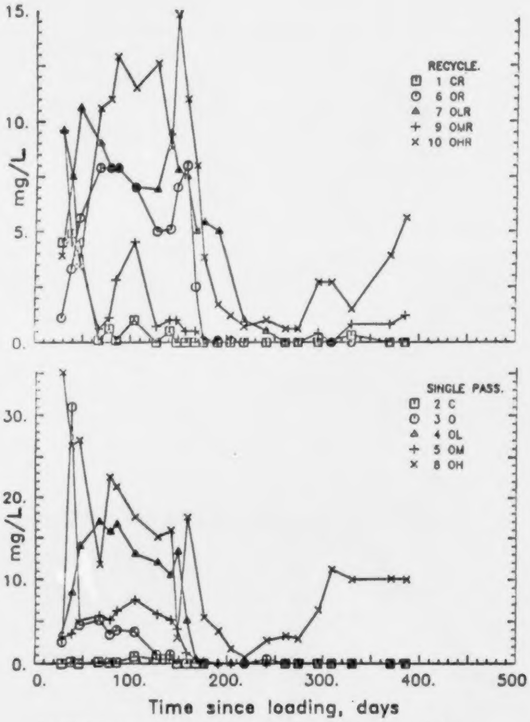

Figure 9. Leachate Pb concentrations for recycle and single pass landfill columns.

Based on known solubility equilibria (5,6), a predominance area diagram has been constructed in Figure 10 for the important lead species under the prevailing pH conditions. From this diagram, it is apparent that the solid

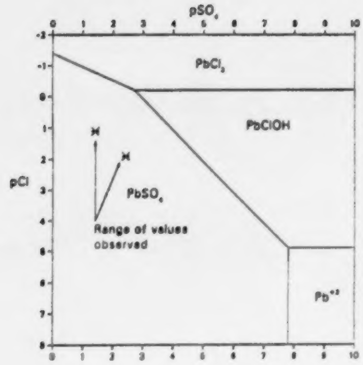

Figure 10. Predominance area diagram for Pb for the recycle and single pass landfill columns.

species controlling lead solubility in the absence of sulfide is $PbSO_4$. Therefore, in consideration of the complexity of equilibria for this system, the low leachate lead concentrations are reasonably consistent with sulfide as the precipitant anion, while the more recent higher concentrations are well within the range expected in the presence of sulfate control.

When coupled with the importance of biological mediation, the results suggest the possibility of very limited initial sulfate reduction, but of sufficient magnitude to control lead solubility. Thereafter, possible heavy metal or acid inhibition may have retarded further generation of sulfide, thereby shifting lead solubility control to the sulfate ion. As the experiments progress and methane fermentation is initiated with the further production of sulfide, solubility control for lead may again shift to sulfide. The onset of methane fermentation with its concomitment requirements for increasingly low redox potentials will also continue to sustain mercury in the metallic state.

Changes in Organic Priority Pollutants

Although the results of analyses on the organic priority pollutants added to the test columns have not yet revealed as dramatic an impact on leachate quality, the waste mass appears to be influencing release consistent with solubility and octanol/water partition coefficients (K_{OW}) as summarized in Table 3. Since K_{OW} is a measure of the tendency of a compound to partition between water and a hydrophobic phase, with increasing log K_{OW} indicating increasing hydrophobicity, each of the listed compounds could be inspected relative to their ability to dissolve in the leachate and to be sorbed by the refuse mass. Consequently, the highly soluble compounds would be expected to appear rapidly in the leachate at relatively high concentrations, while the less soluble would tend to be retained.

To test this hypothesis within the landfill setting, it was necessary to inspect the order and intensity of appearance of the organic priority pollutants, taking into account the position of loading (near the bottom of each column), the possibility of volatilization, and the mode of operation (single pass or recycle). As indicated in Table 4, all organic priority pollutants with vapor pressures greater than 1.9 kPa (Table 3) have been observed in the gas phase of the columns at least once. Gas phase transfer, although minimal due to low gas evolution under acid formation conditions, was most frequently detected for trichloroethene and dibromomethane. To assess the magnitude of this transfer, gas phase concentrations and masses have been estimated for these two compounds in Table 5. Based upon this analysis, gas phase transfer was not yet considered significant, but would possibly be more so when methane fermentation with gas evolution and stripping of volatile compounds is established.

With respect to the leachate analyses of Table 6, lindane and dioctyl phthalate did not appear during the first year of column operation, whereas the more soluble trichloroethene and dibromomethane appeared almost immediately. However, as time passed, these latter compounds eventually disappeared. In comparison, the phenolic compounds (2,4-dichlorophenol and nitrophenol), although quite soluble, have been observed only at relatively low concentrations. Similarly, 1,2,4-trichlorobenzene, with its low solubility and high log K_{OW}, has been detected at low concentrations, whereas naphthalene, being only moderately soluble and fairly hydrophobic, consistently appeared at low to moderate concentrations.

TABLE 3. PHYSICAL-CHEMICAL CHARACTERISTICS OF ORGANIC PRIORITY POLLUTANTS

Organic Compound	Molecular Weight	Aqueous Solubility mg/L		Vapor Pressure at 100°, kPa	Log Octanol/ Water Partition Coefficient, K_{ow}
1,1,2-Trichloroethene	131.4	1,100	(20°C)	150	2.29
Dibromomethane	173.9	11,700	(15°C)	101	1.45
1,4-Dichlorobenzene	147.0	49	(22°C)	8.1	3.38
Nitrobenzene	123.1	1,900	(20°C)	3.3	1.85
2-Nitrophenol	139.1	2,100	(20°C)	2.54	1.76
Naphthalene	128.2	26.2	(20°C)	2.5	3.37
2,4-Dichlorophenol	163.0	4,500	(20°C)	1.9	2.75
1,2,4-Trichlorobenzene	181.5	19	(22°C)	3.3	4.04
Lindane	290.9	17	(24°C)	0.17	3.72
Dieldrin	381.0	0.1		2.39×10^{-5} (25°C)	>5.6
Dioctyl phthalate	391.0	0.285	(24°C)	0.0002	5.2
Hexachlorobenzene	284.8	0.11	(24°C)	133 (114.4°C)	5.61

Adapted from Verschueren (7).

TABLE 4. FREQUENCY OF OCCURRENCE OF ORGANIC PRIORITY POLLUTANTS IN GAS TRAPS

Organic Compound	Frequency of Detection	
	Samples	Percent
1,1,2-Trichloroethene	44	92
Dibromomethane	32	67
2,4-Dichlorophenol	25	52
2-Nitrophenol	13	27
Nitrobenzene	10	21
1,4-Dichlorobenzene	22	46
1,2,4-Trichlorobenzene	1	2
Naphthalene	14	29
Hexachlorobenzene	3	6
Lindane	ND	0
Dieldrin	ND	0
Dioctyl phthalate	ND	0

ND = Not detected.
*Total of 48 samples from gas traps obtained throughout experiments to Day 400.

TABLE 5. SUMMARY OF GAS PHASE TRANSFER OF TRICHLOROETHENE AND DIBROMOMETHANE

Landfill Column*	Trichloroethene			Dibromomethane		
	Average Concentration, ppb	Range of Concentration, ppb	Total Mass Volatized, µg	Average Concentration, ppb	Range of Concentration, ppb	Total Mass Volatized, µg
1(CR)	6.48	BDL - 39.1	300	0	-	0
2(C)	0.49	BDL - 2.53	6	0	-	0
3(O)	185	6.25 - 820	3,800	0.81	BDL - 4.85	22
4(OL)	764	585 - 958	2,600	18.2	BDL - 91.2	82
5(OM)	385	10.3 - 1250	4,000	5.1	BDL - 26.2	71
6(OR)	137	13.8 - 878	1,500	57	BDL - 238	830
7(OLR)	247	58.7 - 903	720	71	BDL - 354	280
8(OH)	267	55.1 - 607	2,160	2.0	BDL - 8.54	21
9(OMR)	378	87.6 - 1182	2,020	0.88	BDL - 4.52	6
10(OHR)	757	12.3 - 3500	8,900	0.33	BDL - .86	5

*As on Table 1.

TABLE 6. ELUTION ORDER FOR ORGANIC PRIORITY POLLUTANTS

Compound	First Day Observed in Leachate		Final Day Observed in Leachate		Maximum Concentration Observed in Leachate, mg/L	
	Single Pass	Recycle	Single Pass	Recycle	Single Pass	Recycle
1,1,2-Trichloroethene	29	29	*	*	16	14
Dibromomethane	29	29	478	453	3	5
Nitrobenzene	29	29	239[a]	260[d]	26	28
1,4-Dichlorobenzene	29	36	85[b]	85[c]	5	6
2-Nitrophenol	36	36	288[a]	288[e]	11	2
2,4-Dichlorophenol	36	36	*	*	15	2
Naphthalene	36	36	*	*	7	7
1,2,4-Trichlorobenzene	54	43	*	*	0.8	0.9
Dioctyl phthalate	64	64	400	473	2	1
Lindane	64	111	410	*	0.5	0.3
Hexachlorobenzene	410	389	410	453	0.15	0.2
Dieldrin	ND	ND	ND	ND	-	-

ND = Not detected.
*Currently present.
[a] Observed in leachate from two columns subsequently.
[b] Reappeared in leachate on Day 260.
[c] Reappeared in leachate on Day 355.
[d] Reappeared in leachate on Day 370 and after Day 480.
[e] Reappeared in leachate on Day 488.

Although it is difficult to establish potential attenuation mechanisms for the organic priority pollutants in terms of physical-chemical and/or biologically mediated interactions, all have now appeared in the leachates from the test columns and some notion of elution order can be established. Combining the data of Table 3 with those of Table 6 suggests that K_{OW} is a useful parameter for establishing elution patterns. Hence, all compounds with log K_{OW} values of 3.4 or lower were present in the leachate no later than Day 36, between Days 40 and 120 for log K_{OW} ranging from 3.7 and 5.2, and at Day 400 or longer for log K_{OW} in excess of 5.6. Additional examination of these elution patterns will be necessary to provide a more comprehensive understanding of these changes and the possible influences of a transition from acid formation to methane fermentation under either single pass or recycle operations. The opportunity for reinjection of leached compounds for repartitioning or possible extended attenuation in the case of the recycle columns is expected to account for some of the alternating elution patterns detected.

CONCLUSIONS

Preliminary analyses of results from investigations on the codisposal of priority pollutants with municipal refuse in simulated landfill columns, operated under the influence of single pass leaching or leachate recycle, have begun to suggest possible attenuating mechanisms. The removal of heavy metals is strongly influenced by the loading intensity, the physical and chemical characteristics of the admixed waste and leachate transport medium, the progress of microbially mediated stabilization, and the presence and availability of inhibitors and/or reactive species.

The reducing environment helps to determine metal speciation and reaction potential in terms of possible precipitation or complexation. Metallic mercury is the suggested form of that metal, with a potential for release through the leachate or gas phases. Sulfur species are implicated as controlling lead mobility either through precipitation or complexation. The distribution of oxidized or reduced sulfur is determined by the opportunity for biologically mediated reduction which may be itself inhibited by the heavy metal loadings, acid pH conditions and unfavorable redox potentials. These contingencies should become more evident as the results of the heavy metal loadings are compared under the succeeding methane fermentation phase of landfill stabilization.

The impact of the simulated landfill conditions on the release or possible attenuation of the organic priority pollutants remains uncertain, but several logical patterns are beginning to emerge. Solubility and/or reaction in the waste or leachate and gas transport media in accordance with physical-chemical properties is somewhat predictable, log octanol/water partition coefficient being particularly useful. Alternating periods of appearance and disappearance of organic priority pollutants in the leachate or gas may reflect flow patterns established by single pass or recycle operations as well as the potential for physical-chemical partitioning and possible bioattenuation. As the microbially mediated processes of landfill stabilization become more actively established under the ensuing methane fermentation phase, the effect of the imposition of the loadings and the most probable assimilative mechanisms will become clearer.

ACKNOWLEDGEMENTS

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FIELD VERIFICATION OF FMLS--ASSESSMENT OF AN UNCOVERED UNREINFORCED 60-MIL EPDM LINER AFTER 18 YEARS OF EXPOSURE

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ABSTRACT

Samples of a 60-mil vulcanized ethylene propylene rubber (EPDM) flexible membrane liner (FML) were recovered for analysis and physical testing from different locations within a basin that was being decommissioned after 18 years of service as an emergency pond for "red-water." Observations on the in-place uncovered liner, description of the sampling procedure and collection of the samples, and results of the laboratory testing of the samples are presented.

The properties of the liner samples varied significantly depending on the location in the basin from which they were taken. Samples taken from the liner on the dike slope facing south had less extractables (i.e., oily plasticizers) and generally had higher tensile strength and modulus than the reference FML. The samples taken from the liner on the bottom of the basin had high extractables and properties comparable to those of the reference. As no retained sample or analytical and physical test data on the original unexposed sheeting were available for comparison, data on a 1972 EPDM liner were used for reference.

No failures were observed in the factory seams of the in-place liner. Most of the field seams on the slopes opened, resulting in sloughing of the liner. Those field seams that were high on the slope showed an apparent increase in crosslinks of the adhesive; however, the adhesive retained tack in most of the tested field seams, indicating low cure.

Rodents had gnawed holes in the liner from the top surface in the upper slope areas. There was no indication that the rodents had burrowed below the liner and gnawed from beneath the liner. The design of the anchor trench using wooden planks was unsatisfactory, as many of the panels of sheeting pulled out.

INTRODUCTION

Considerable laboratory test data have been generated over the past several years with respect to the properties of FMLs and their chemical compatibility with hazardous liquids and waste liquids. Such data are continually being generated in research and in EPA 9090 liner/waste compatibility tests. On the other hand, the data that are available on the effects on FMLs in service in waste containment, particularly data in the open literature, are limited. Several studies have been undertaken by the EPA to assess liners that have been removed from service (Roberts et al, 1983; Nelson et al, 1985; Emcon Associates, 1983; Matrecon, 1983); however, these studies are relatively few in number and the exposures are limited, both with respect to length of service and severity of exposure. Much more information on the field performance of lining materials in service needs to be obtained and analyzed in order to develop correlation between laboratory test data and actual performance. Such data are also needed to set criteria for performance or magnitude of the changes in properties that will affect performance. These criteria are needed for use in assessing the results of EPA 9090 liner compatibility tests.

An opportunity arose to assess the effects on an EPDM liner of 18 years of exposure in a surface impoundment when an Emergency "Red-water" Basin located at the Joliet Army Ammunition Plant in Joliet, Illinois, was scheduled to be decommissioned. Arrangements were made through the Hazardous Waste Engineering Research Laboratory of EPA in Cincinnati for Matrecon to observe some of the cleanup of the basin and the removal of the lining material, and to collect samples of the EPDM liner which had been in service under relatively mild conditions that may not be typical of most landfills or surface impoundments.

The objective of the work was to assess the overall condition of the uncovered unreinforced FML after 18 years of exposure to the waste liquid and weather, and to assess the overall condition of the basin below the EPDM liner.

This paper presents a description of the basin at the time of sampling, a description of the sampling procedure, observations made during the sampling of the liner, and the results of the laboratory testing of the exposed samples.

DESCRIPTION OF THE BASIN AND THE LINER

The basin was constructed in late 1967 and early 1968 to act as a surge pond for "red water" produced as a waste from TNT production. The pond covered an area of 3.1 acres and contained "red water" waste liquid, which was usually concentrated by evaporation and then disposed of by incineration. It must be recognized that the composition of the wastewater that was contained was highly variable with time as the basin was used intermittently. The constituent concentration for selected analytes from a sample collected on May 28, 1981 is presented in Table 1.

TABLE 1. COMPOSITION OF SURFACE WATER SAMPLE[a]

Analyte	Concentration (µg/L)
TNT-Related Organics Compounds	
2,4,6-Trinitrotoluene (TNT)	<0.29
2,6-Dinitrotoluene (DNT)	196.0
2,4-Dinitrotoluene (DNT)	1.00
2-Nitrotoluene	5.7
1,3,5-Trinitrobenzene	<2.2
Anions	
Nitrite	<250
Nitrate	433,000
Sulfate	6,690,000
Phosphate	390
Heavy Metals	
Arsenic	<13.0
Cadmium	8.8
Chromium (hexavalent)	1.5
Chromium (total)	125.0
Copper	141.0
Iron	5,360.0
Lead	40.2
Manganese	195.0
Mercury	<0.35

[a]Sample number: SW109; sample date: May 28, 1981.

Source: Tom Erdman of the Joliet Army Ammunition Plant.

The basin was last used during TNT production for the Viet Nam war and was dismantled in May 1985, because it was no longer needed. The capacity of the basin was 4.06 million gallons. It had an average depth of about 5 ft, and the dike slope was 3:1. The liner was an unreinforced EPDM FML of 60-mil nominal thickness. It was uncovered, that is, no soil cover was placed on the liner. Figures 1 and 2 present a panaromic view from the southeastern corner of the basin at the time the liner was being sampled. The water table in the area appeared to have been about the same as that of the basin bottom as a partially-filled water drainage ditch ran along the outside of the dike on the north and the east sides.

Most of the field seams along the basin slopes failed, but, from what could

Figure 1. Part 1 of the panoramic view of the basin at the time liner samples were collected. View is from the southeastern corner of the basin. Note the sloughing from the liner and the hosing of the sludge to maintain its slurry consistency to make it easy to pump.

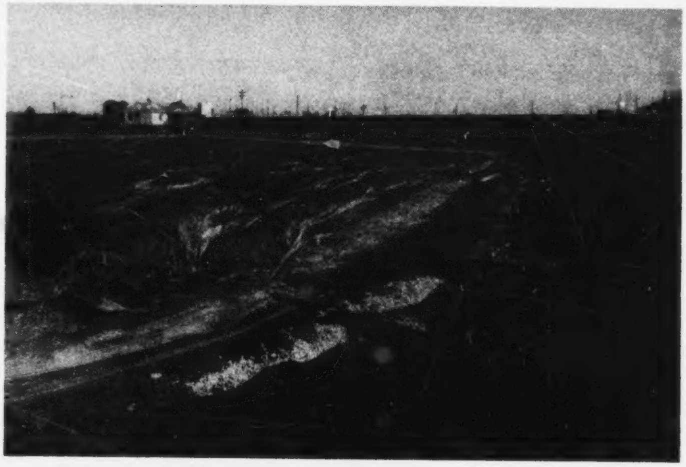

Figure 2. Part 2 of the panoramic view of the basin at the time the liner samples were collected. View is from the southeastern corner of the basin. Note the anchor trench failure and the field seam failures.

be observed of the basin bottom, the field seams were mostly intact; we did not observe a single failure of the factory seams. (Figure 3 shows a partially-opened field seam on the slope.)

Figure 3. Partially-opened field seam on the slope. Note the apparent tension and shrinkage away from the seam. Nearby factory seams are intact.

The anchor trench along the berm top was completely inadequate for anchoring (Figure 4) the top of the liner. In combination with the failure of the field seams, this poor anchorage resulted in large sections of the basin slopes not being covered by the liner. The extent of failure of the FML is documented in the site photographs (Figures 1, 2, and 5).

Gas generation below the liner resulted in the formation of "whales" or areas of the liner which lifted off the floor of the basin. No means for bleeding off the gas appeared to have been incorporated into the pond design. It was reported that these "whales" were punctured to release trapped gases shortly before the liner sampling was started. An attempt had been made earlier to relieve the trapped gases by attaching vent pipes to the liner, but these vents appear to have been ineffective.

The bulk of the liquid in the basin had been removed before the sampling was started and the cleanup of the sludge (which was drying) was underway. By dragging a sled across the bottom, the sludge could be kept wet (Figures 1 and 2) so that it could be handled as a slurry. It was also felt that the residual TNT in the sludge would be less active when wet.

SAMPLING OF LINERS FOR TEST

For assessing the overall effects of exposure and aging on the properties of an exposed liner from a lined surface impoundment, it is desirable to obtain samples that have been exposed to a range of conditions from the mildest condition that is believed to exist in a given impoundment to that believed to be the most severe exposure (Nelson et al, 1985). To meet these requirements, we tried to:

- Obtain a 2-ft wide "strip" sample that extended from the anchor trench down the slope and onto the bottom of the impoundment. The location should be on the north side, facing south. This sample would yield sufficient material for testing the principal areas of exposure that a liner would encounter in an impoundment, from the top to the bottom.

- Collect several samples of factory and field seams.

- In addition to the "strip" sample, collect samples of the completely submerged liner with seams, particularly at the lowest point of the liner, e.g., the sump area.

- Collect any samples that showed abnormal exposure or other abnormalities.

Figure 4. Anchor trench construction. This photograph shows the top of Sample A immediately prior to cutting.

Figure 5. Failure of the anchor trench due to the pullout of the membrane.

Four major liner samples were obtained and were designated Samples A, B, C, and D. In addition, seven smaller samples containing holes, apparently caused by rodents, were also collected (Figure 6).

The reason why each of the major samples was taken are discussed briefly below:

- Sample A was the major sample from this liner. It was taken from the northeastern dike (southern exposure) and extended from the anchor trench at the top of the dike, down the dike, and on to the basin bottom. A factory seam extended most of the sample length and a field seam extended into the bottom section. Due to its size, the strip was cut into three sections. The schematic drawing (Figure 7) shows the different sections and areas from which test specimens were drawn. The drawing also shows the seams and the locations that were tested.

- Sample B included a field seam which was partly intact and partly failed. It was taken from the northeastern dike between Sample A and the northeast corner of the basin.

- Sample C was from the basin bottom. Before collection, it was covered with very wet sludge and exposed to very wet mud on the underside. A small strip cut from the liner adjacent to Sample C was collected for volatiles determination.

- Sample D included a partly intact/partly failed field seam from a "whale." Sample D was chosen because "whales" are considered to be sites of stress on the liner and because of the presence of a field seam.

The locations where the samples were collected are shown in Figure 8, a simplified drawing based on the "as built" drawing of the basin.

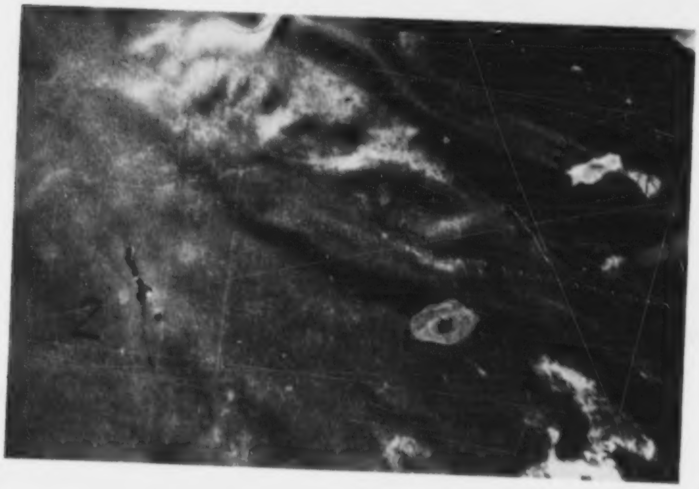

Figure 6. Holes gnawed by rodents in the liner at the top of the slope. The 1 and 2 refer to samples cut from the liner.

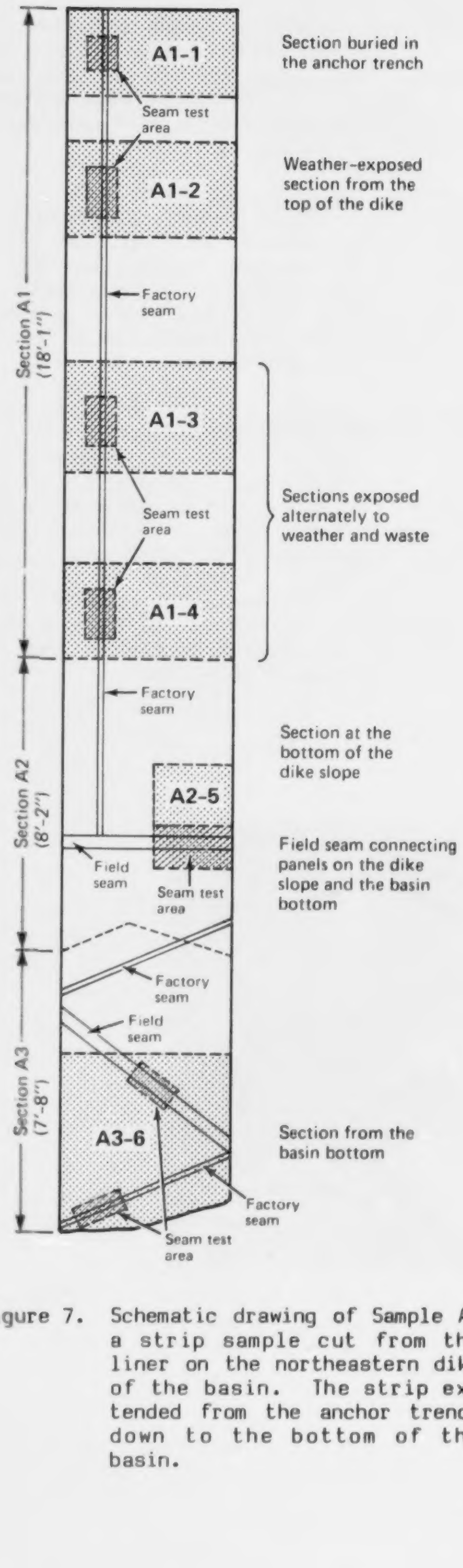
A1-1
Section buried in the anchor trench
Seam test area
A1-2
Weather-exposed section from the top of the dike
Factory seam
Section A1 (18'-1")
A1-3
Seam test area
Sections exposed alternately to weather and waste
A1-4
Factory seam
Section at the bottom of the dike slope
Section A2 (8'-2")
A2-5
Field seam connecting panels on the dike slope and the basin bottom
Field seam
Seam test area
Factory seam
Field seam
Section A3 (7'-8")
A3-6
Section from the basin bottom
Factory seam
Seam test area

Figure 7. Schematic drawing of Sample A, a strip sample cut from the liner on the northeastern dike of the basin. The strip extended from the anchor trench down to the bottom of the basin.

No retained sample of the original liner was available for use as a baseline reference. The top portion of Sample A, which was buried in the shallow anchor trench on top of the dike, probably had only a modest exposure to either waste or sun, but it appeared to have aged and lost extractables and thus could not be used as a baseline reference.

The temperature on the day the samples were collected was in the mid-70's. The weather varied from clear in the morning, to cloudy in the early afternoon, to clear again in the late afternoon.

The samples cut from the liner were kept as cool as possible, particularly those that were removed from under sludge or soil (i.e., from the anchor trench) or had been below the liquid. The samples were washed without scrubbing to remove loose material, then rolled and placed in aluminum tubes. A small amount of water was added to each of the tubes that contained moist liners and the tubes were sealed at the ends with metal caps.

TESTING OF SAMPLES

Analytical and Physical Properties

The liner samples were photographed and measured at the laboratory; Sample A, the "strip" sample, was tested in the following areas, as shown in Figure 7.

- Section A1, the upper section of the "strip", was tested in four areas. Test areas were designated Samples A1-1, A1-2, A1-3, and A1-4. These samples had been exposed in the anchor trench, at the top of the slope, at mid-slope, and at the toe of the slope, respectively.
- Section A2 was tested for analytical and physical properties in an area that had been at the bottom of the slope. The test area was designated Sample A2-5.
- Section A3, which had been exposed at the bottom of the basin, was tested for physical properties. The test area was designated Sample A3-6.

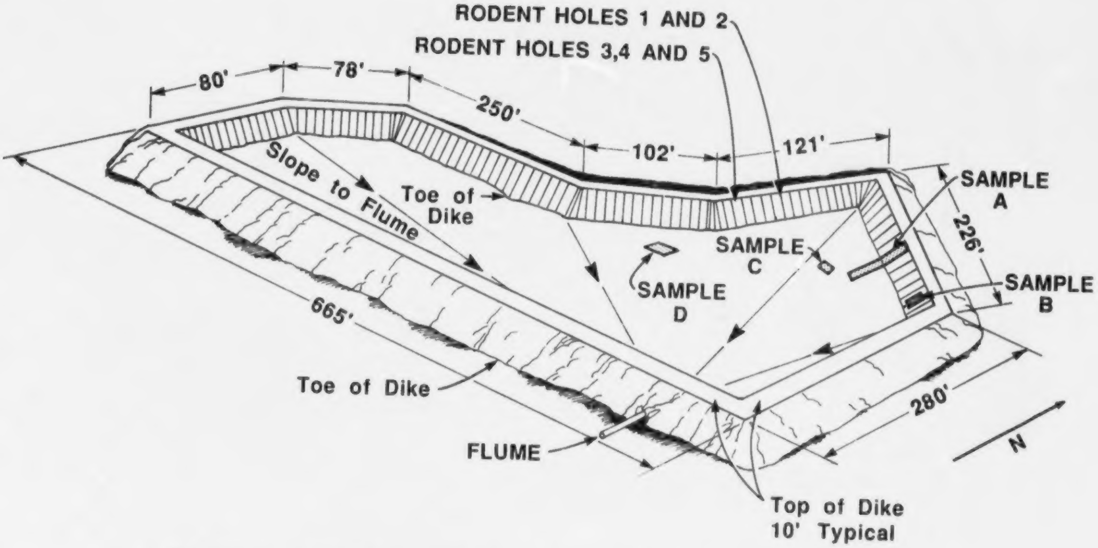

Figure 8. Schematic drawing of the basin showing the location where the liner samples were collected.

The other three samples were tested as follows:

- Sample B, taken at a field seam, was tested in two areas designated Samples B1 and B2 which correspond to two different layers of the same sheeting. Sample B1 was exposed to the weather and possibly waste; Sample B2 was the underflap part of the intact portion of the field seam.

- Sample C--the strip taken adjacent to Sample C from the bottom of the basin was analyzed immediately for volatiles upon receipt at the laboratory. Physical tests and additional analyses were later performed on the main portion of Sample C.

- Sample D, cut from a "whale", was tested for analytical and physical properties and the intact part of the seam was tested in the peel mode.

The properties of the exposed FMLs that were measured and the specific test methods that were used are presented in Table 2. The results of the testing are presented in Table 3.

TABLE 2. PROPERTIES AND TEST METHODS

Property	Test method[a]
Tensile properties	ASTM D412
Tear strength	ASTM D624
Puncture resistance	FTMS 101C, Method 2065
Hardness	ASTM D2240
Volatiles content	MTM 1
Extractables content	MTM 2 (with methyl ethyl ketone)
Ash content	ASTM D297
Specific gravity	ASTM D792
Thermogravimetric analysis	Haxo (1983)

[a] ASTM = American Society for Testing and Materials; FTMS = Federal Test Method Standard; MTM = Matrecon Test Method (Matrecon, 1983).

Seam Strength

Many of the areas tested for physical properties included factory or

TABLE 3. PROPERTIES OF 60-MIL EPDM LINER SAMPLES COLLECTED FROM THE EMERGENCY "RED-WATER" BASIN

			Strip Sample A						Liner on slope with field seam				
							Basin bottom						
Property	Direction of test	Prelim-inary Sample[a]	Anchor trench A1-1	Top of slope A1-2	Mid-slope A1-3	Toe of slope A1-4	A2-5	A3-6	Top layer B1	Bottom layer B2	Basin bottom C	Top of "Whale" D	1972 EPDM liner[b]
Analytical properties													
Volatiles, %		0.88	...	1.19	1.35	0.94	0.56[c]	...	0.77	0.72	0.77[c]	0.85	0.38
Extractables[d], %		15.9	13.52	14.65	16.31	16.56	21.60[e]	21.28	14.26	17.13	21.62	17.72	23.41
Ash, %		...	7.90	...	...	...	7.3	...	...	7.90	7.24	8.04	6.78
Specific gravity		...	1.218	...	...	...	...	1.181	...	1.203	1.180	1.183	1.173
Physical properties													
Tensile at break, psi	Machine	1870	1865	1810	1825	1835	1750	1765	1925	1765	1755	1815	1635
	Transverse	...	1860	1775	1765	1755	1735	1725	1765	1730	1730	1805	1550
Elongation at break, %	Machine	375	370	280	330	355	415	400	275	345	390	370	520
	Transverse	...	410	290	355	370	455	410	265	350	420	400	500
Stress at 100% elongation, psi	Machine	515	640	790	640	605	445	450	800	505	445	525	350
	Transverse	...	600	725	545	525	390	400	700	460	380	465	320
Stress at 200% elongation, psi	Machine	1150	1230	1480	1290	1260	1000	1015	1555	1150	1045	1165	800
	Transverse	...	1140	1390	1180	1130	890	935	1425	1090	925	1040	740
Tear strength, ppi	Machine	193	190	160	160	170	190	170	155	170	175	180	206
	Transverse	...	185	150	165	165	180	170	150	170	175	180	211
Puncture resistance													
Thickness, mil		62.5	...	55.6	55.0	53.7	56.5	63.0	69.7	71.3	61.5	56.5	60
Maximum stress at puncture, lb		76.2	...	67.4	53.0	51.8	54.0	58.5	89.0	79.0	62.7	56.6	56.9
Elongation at break, in.		1.20	...	1.09	1.07	1.06	1.17	1.21	1.00	1.14	1.31	1.15	1.46
Maximum stress, normalized for 100-mil thickness, lb		122.0	...	121.2	96.4	96.5	95.6	92.9	127.7	110.8	102.0	100.2	94.8
Hardness, Duro A points													
1-second reading		70	69	72	68	67	64	65	71	65	63	69	...
5-second reading		67	66	70	66	64	63	63	67	61	61	66	57

[a] Preliminary sample received 1-5-84. Direction of test uncertain but is believed to be the machine direction; sample taken from top of slope by Mr. T. Erdman of the Joliet Army Ammunition Plant.

[b] Baseline reference--Liner No. 8 (Haxo et al, 1985).

[c] Values of 0.83% and 1.23% were obtained, respectively, on small samples of A2-5 and C that had been collected and sealed in small tins to prevent loss of volatiles.

[d] Extractables were determined with methyl ethyl ketone.

[e] Value of 22.28% was obtained on the small sample of A2-5 collected for volatiles determination.

field seams that were tested for seam strength in shear and peel modes. The location and type of seam samples that were tested for seam strength are indicated in Table 4.

Seam strength in shear mode was measured in accordance with ASTM D882 and D3083, modified for testing exposed FMLs. Testing in peel mode was performed in accordance with ASTM D413 in 90° peel. In both modes of testing, 1-in. wide strip specimens were tested at a jaw separation rate of 2 inches per minute. The results of the seam testing are presented in Table 4.

SEAMS

The seams in the liner were prepared both in the controlled environment of the factory and in the uncontrolled outdoor environment of the field. Roll stock of EPDM sheeting was manufactured and fabricated into large panels at the factory that were then installed in the basin. Vulcanized seams were made to join the sheeting into panels at the factory, while vulcanizable adhesives were used to join the panels to form the liner in the field.

The vulcanized factory seams appeared, after exposure to "red water" and weather, to be similar to new factory seams. The factory seam was 3.2-in. wide and the edges of both the top and bottom sheets were beveled to a thickness of about 30 mils up to 0.75 inches in from the edge of each sheet. The field seam was 6-in. wide and was bonded with a vulcanizable adhesive. A low-temperature vulcanizable tape was placed along the edge of the top sheet. In addition to its function in bonding the sheets together, the tape also served to round the edge of the top sheet. However, many of the field seams displayed an opening in the tape along and adjacent to the edge of the top sheet. This opening

TABLE 4. SEAM STRENGTH IN SHEAR AND PEEL MODES OF 60-MIL EPDM SEAM SAMPLES COLLECTED FROM THE EMERGENCY "RED-WATER" BASIN

	Strip Sample A (type of seam)					A3-6				
Seam test	Anchor trench A1-1 (Factory)	Top slope A1-2 (Factory)	Mid-slope A1-3 (Factory)	Lower slope A1-4 (Factory)	On basin bottom A2-5 (Field)	(Factory)	(Field)	High on slope B1/B2 (Field)	On basin bottom C (Factory)	Top of "Whale" D (Field)
Seam strength in shear[a]										
Maximum strength[b], ppi	...	64.0	65.6	68.1	69.2	...	...	64.4	...	...
Strength at break, ppi	...	64.0	65.6	68.1	69.2	...	...	64.4	...	...
Locus of break[c]										
FTB[d]	...	0	0	1 SE	0	...	...	0	...	...
Non-FTB[d]	...	5 AD	5 AD	4 AD	5 AD	...	...	3 AD	...	...
Seam strength in peel[e]										
Maximum strength, ppi	11.7	6.5	7.8	8.2	9.2	10.1	8.8	17.6	8.7	8.9
Locus of break[c]										
FTB[d]	0	0	0	0	0	0	0	0	0	0
Non-FTB[d]	5 AD	5 AD	5 AD	5 AD	5 AD	5 AD	5 AD	5 AD	5 AD	5 AD

[a] ASTM D882/D3083, modified; five specimens tested per sample, except where otherwise noted. Two specimens of Sample B2 slipped in the clamps during testing; results declared void.

[b] Maximum value corresponds to tensile strength at break for all specimens tested.

[c] Locus-of-break determined from the following code:

Locus of Break	Description	Classification
CL	Break at clamp edge	FTB[e]
SE	Break at seam edge	FTB[e]
BRK	Break in sheeting	FTB[e]
AD	Break in adhesion	non-FTB[e]

[d] FTB = film-tear bond.

[e] ASTM D413, modified; five specimens tested per sample except where noted otherwise.

may have been caused by differential shrink and swell of the sheeting and the adhesive.

SELECTION OF A BASELINE REFERENCE

No retained sample of the liner was available that could be used as a baseline reference. The samples that were recovered from the basin were 18 years of age; consequently, there was a question as to whether any of these samples was suitable for use as a baseline reference. However, we had data on EPDM FMLs that had been produced in 1972 and tested in earlier work performed by Matrecon for the EPA on a study of liners for municipal solid waste landfills (Haxo et al, 1982; Haxo et al, 1985). A review of the analytical results for an FML produced in 1972 indicated that it was essentially the same as that of the liner installed in the basin in 1967. A comparison of analytical properties of the 1972 EPDM liner with the liner recovered from the basin is given in Table 5. The data as a group constitute a fingerprint of the liner, such as described by Haxo (1983).

The physical properties for the 1972 membrane are presented in Table 3. Tensile strength, stress at 100% elongation, and puncture resistance are comparable to the data obtained on the liner taken from the basin, assuming somewhat higher extractables content. Using these data, one has a baseline reference against which to compare the effects of the exposure on the liner samples recovered from the basin.

RESULTS AND DISCUSSION

Data on the samples taken from the various sections of the "strip" sample can be used to assess the effect of the different exposures from the top to the bottom of the basin. Some of the basic conclusions that can be drawn are:

- The extractables decrease with increasing distance from the bottom of the basin which has been under "red water" or sludge.
- The sheeting on the top part of the slope, which was exposed to the sun, contains about one-third less of oily plasticizer than was in the sheeting on the floor of the basin. The latter sheeting has the highest extractables values. These high values approximated that of the "baseline reference" (i.e., the 1972 EPDM liner). Also, the tensile strength, modulus (stress at 100% elongation), and puncture resistance values tend to increase with decreasing extractables, that is, with distance up from the bottom of the basin, as is shown in Figures 9 through 11. On the other hand, the elongation at break decreases as the extractables decrease during the exposure, as shown in Figure 12.

TABLE 5. COMPARSION OF ANALYTICAL PROPERTIES OF EXPOSED SAMPLE AND BASELINE REFERENCE

Analysis	Joliet Sample C	1972 Liner No. 8
Extractables[a], %	21.62	23.41
Thermogravimetric analysis:		
Polymer + oils, %	57.2	57.4
Polymer (calculated)[b], %	35.6	34.1
Oil (from extractables), %	21.6	23.4
Carbon black, %	35.2	35.0
Ash, %	7.6	7.5
Total	100.0	100.0
Ash, %	7.24	6.78
Specific gravity	1.183	1.173

[a] Extractables consist of oils + extractable curatives and antidegradants (determined with methyl ethyl ketone).

[b] Calculated by subtracting the extractables from the thermogravimetric analysis (TGA) determination for polymer + oil.

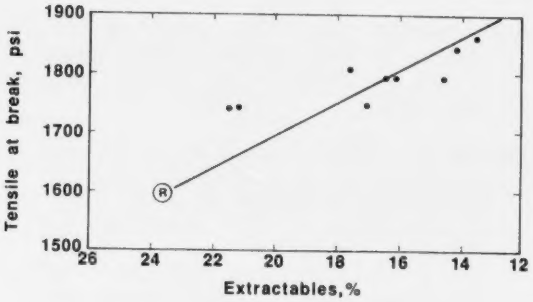

Figure 9. Tensile at break of the samples of exposed FMLs as a function of their extractables. Tensile data are the averages of the values obtained in both machine and transverse directions. The samples with the low values for extractables were cut from the liner at the top of the slope. Those with the high values were cut from the liner on the bottom. R = Baseline Reference EPDM, produced in 1972.

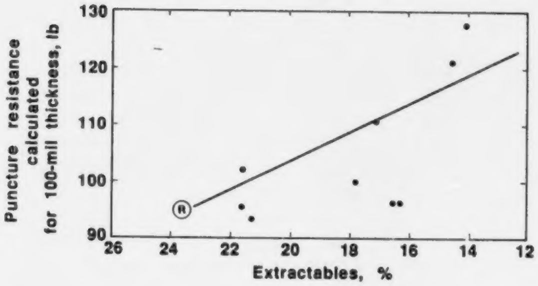

Figure 11. Puncture resistance of the samples of exposed FMLs as a function of their extractables. Puncture resistance is the maximum stress value calculated for 100-mil thickness of the FML. The samples with the low values for extractables were cut from the liner at the top of the slope. Those with the high values were cut from the liner on the bottom. R = Baseline Reference EPDM, produced in 1972.

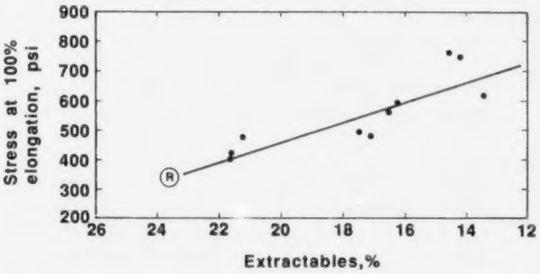

Figure 10. Stress at 100% elongation (S-100) of the samples of exposed FMLs as a function of their extractables. S-100 data are the averages of the values obtained in both machine and transverse directions. The samples with the low values for extractables were cut from the liner at the top of the slope. Those with the high values were cut from the liner on the bottom. R = Baseline Reference EPDM, produced in 1972.

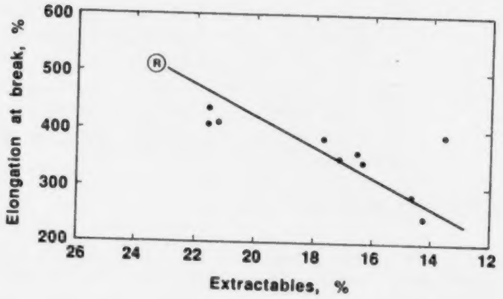

Figure 12. Elongation at break of the samples of exposed FMLs as a function of their extractables. Elongation data are the averages of the values obtained in both machine and transverse directions. The samples with the low values for extractables were cut from the liner at the top of the slope. Those with the high values were cut from the liner on the bottom. R = Baseline Reference EPDM, produced in 1972.

- In the case of sheeting protected at the seams by an upper layer of sheeting, the extractables are greater and the tensile strength, modulus, and puncture resistance are less than those of the upper layer. These differences again appear to reflect the increased plasticizer content of the protected sheeting.

- The factory seam results tend to show increased strength values in both shear and peel modes with increased distance from top to bottom down the slope. The peel adhesion values increased from 6.5 to 10.1 ppi with distance down from the anchor trench; all the failures in the tests were adhesion failures between the sheetings.

- In the case of field seams, there is a difference between the exposure locations. A high value of 17.6 was obtained on an unfailed part of the seam that was high on the slope. This seam had partially failed during exposure. Testing was performed on an unfailed portion of the seam. In this case, the adhesive appeared to have crosslinked more than had the seams in the other locations. In all cases, the preponderant failure was a cohesive failure in the adhesive.

ACKNOWLEDGMENTS

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GEOSYNTHETIC DESIGN CONSIDERATIONS FOR DOUBLE LINER SYSTEMS

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ABSTRACT

The "minimum technological requirements" of the Hazardous and Solid Waste Amendments of 1984 require a double liner system in most hazardous waste land disposal cells and surface impoundments. Ensuing guidance recommended the use of two flexible membrane liners (FML). Each FML in a landfill and the bottom FML in a surface impoundment is covered by a leachate collection/removal (LCR) system to aid in preventing leachate from standing on the FMLs. This paper reviews design considerations for the FML and LCR systems within the double liner system.

Potential failure modes for geosynthetic FMLs and LCRs are described in this paper and design procedures are reviewed for each of the failure modes. Each design procedure calculates the actual service stress or flow conditions and compares this required performance to the limiting performance of the component itself. The limiting performance is typically obtained from laboratory testing. A Design Ratio (DR) is defined as the ratio of the laboratory limiting performance divided by the calculated service performance.

OVERVIEW

On November 8, 1984, the Resource Conservation and Recovery Act (RCRA) was amended by the Hazardous and Solid Waste Amendments (HSWA). Among the provisions that went into effect were minimum technological requirements for hazardous waste land disposal facilities. HSWA requires new units and lateral expansions of existing facilities to use two liners with a leachate collection system above (in the case of a landfill) and between such liners.

Draft EPA Minimun Technology Guidance (MTG) (1,2) for liners and LCRs was published on May 25, 1985. Proposed codification of the MTG is outlined in the Federal Register, Vol.51, No.60, March 28, 1986.

The MTG standard 'double-liner' system for a landfill is shown on Figure 1 and consists of a primary LCR and FML system over a secondary LCR and a composite FML/clay secondary liner. The primary LCR minimizes the amount of leachate that is allowed to stand on the primary FML. The primary FML must be designed to allow no more than de minimis quantities of leachate to pass through the liner. The secondary LCR collects leachate that has passed through the primary FML and in this fashion bears 'witness' to the integrity of the primary FML. The secondary FML/clay liner must be designed to prevent greater than de minimis quantities of leachate from leaving the system during the minimum 30-year post-closure monitoring period.

MTG MINIMUM DESIGN PROPERTIES

The draft MTG provides minimum standards for each of the components within the recommended double liner system. Shown on Figure 1, these are as follows:

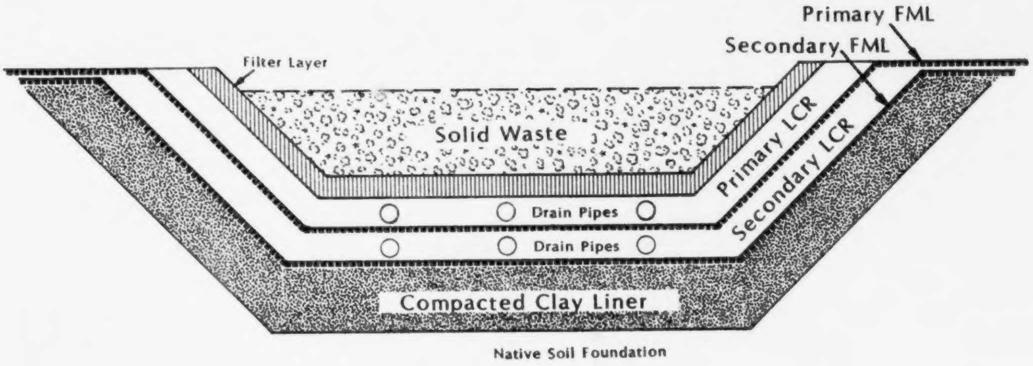


Figure 1 MTG Double-Liner System

o Primary LCR: This system is placed above the primary FML and is separated from the waste by a filter layer. It consists of a minimum of 30 centimeters (cm) of drainage stone having a minimum hydraulic conductivity of 10^{-2} cm/second. A 15-cm thick filter layer is placed between it and the waste, and an internal pipe drain system must be designed to keep less than 30 cm maximum head of leachate acting on the primary FML .

o Primary Liner: The primary liner must be of synthetic material at least 0.75 millimeters (mm) thick. This liner must be designed to allow no more than de minimis quantities of leachate to pass through to the secondary LCR. A composite soil/FML primary liner is allowed under proposed codification.

o Secondary LCR: This witness system has the same minimum properties as the primary LCR but lacks the overlying filter layer.

o Secondary Liner: This is a composite FML/clay liner having an FML with the same minimum thickness as the primary FML, 0.75mm, and an underlying clay having a maximum permeability of 10^{-7} cm/sec and a minimum thickness of 90 cm. The secondary FML is typically of the same material and thickness as the primary FML.

DESIGN CONCEPT - FML

A large number of failure scenarios can be developed for an FML. These failures have in common the generation of large tensile stresses within the FML. Design for these failure mechanisms is based on the stress-strain curves for the particular polymeric material used in forming the FML. For HDPE, the short term stress vs strain curves yield a well defined yield stress while for other polymers such as PVC or CPE, the stress vs strain curves show no distinct yield, Figure 2. Allowable stress limits for such curves are based on a limiting strain level. In both cases, the design philosophy is that a significant amount of FML deformation capacity remains even if the yield stress or strain is reached.

Figure 3 presents four tensile failure mechanisms for an FML. All mechanisms can be quantified on the basis of free-body diagrams that sum the forces or stresses parallel to the surface of the FML. These mechanisms include the following:

o Dead Weight - The self weight of the FML places the FML in tension as it is draped down the sideslope. A high value of DR, greater than 10, insures that excessive elongation of the FML does not occur during placement of the FML. Fortunately, the minimum MTG thickness is normally adequate to generate this level of DR unless extremely steep slopes are present.

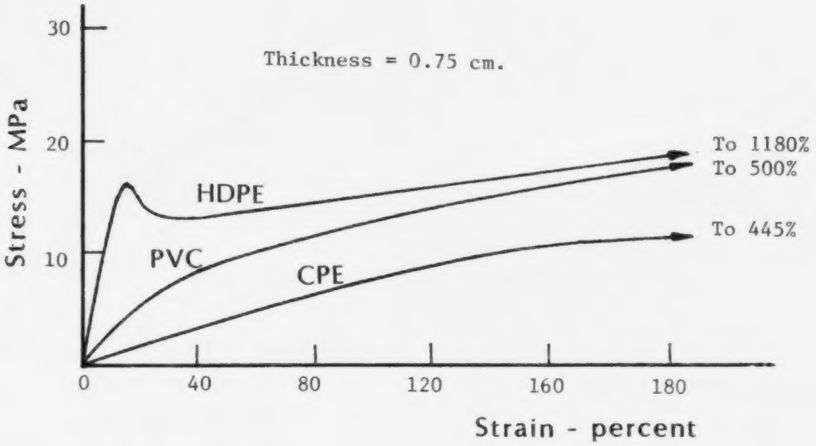


Figure 2 Stress vs Strain for FML

o **Sliding Stability** - Each synthetic layer forming the liner systems forms a potential shear failure plane. Shear is transferred to and from each layer through the friction or adhesion that exists between that layer and the adjacent layers. Shear stresses in excess of that which can be transferred by these surface forces must be resisted in tension by that layer. This reduces the shear stresses transferred to underlying layers.

o Waste Lift Stability - The placement of waste against the liner can produce significant downdrag forces on the liner system. DR values for such problems can easily fall below one (3) if lift heights exceed 3 meters.

o Settlement of Liner - Settlement of the subgrade beneath the liner system can lead to excessive strains within an FML (4). Such settlement could result from the collapse of a drainage line or the uneven densification of poorly compacted soils. The designer must predict subgrade settlements and verify that an adequate DR will exist under these conditions.

With the exception of settlement, these failure mechanisms are also appropriate for evaluation of synthetic LCR systems.

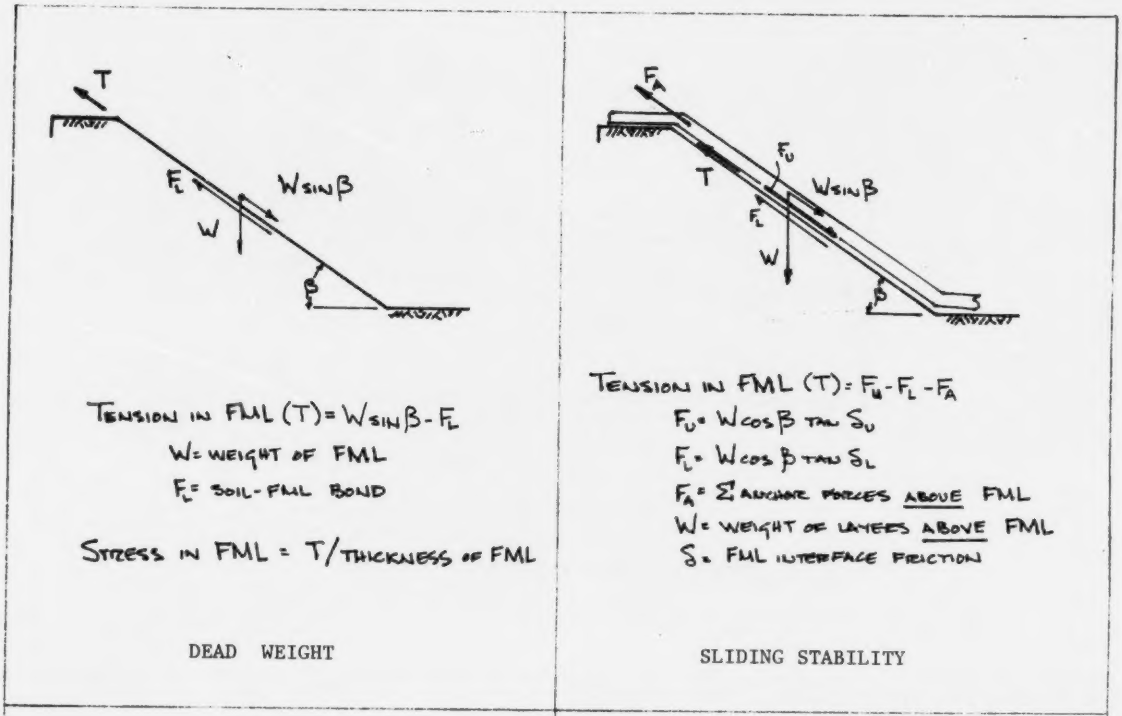
With the exception of the settlement mechanism, all of the above design concerns predict a tension force T acting in the plane of the FML at the shoulder of the sideslope. This force must be resisted by anchorage of the FML beyond the shoulder. Such anchorage is commonly provided by running the FML beyond the shoulder and either burying the end of the FML in a trench or by simply placing sand on top of the FML. Typical FML anchor geometries are shown on Figure 4. The maximum anchorage tension, T_{max}, for the horizontal anchor is given by

$$T_{hor} = \frac{qL\tan\delta}{\cos\beta - \sin\beta\tan\delta} \qquad (1)$$

where δ is the friction angle between the subgrade soil and the FML. The maximum anchorage of the trench system cannot be rigorously calculated at present but can be bounded as follows:

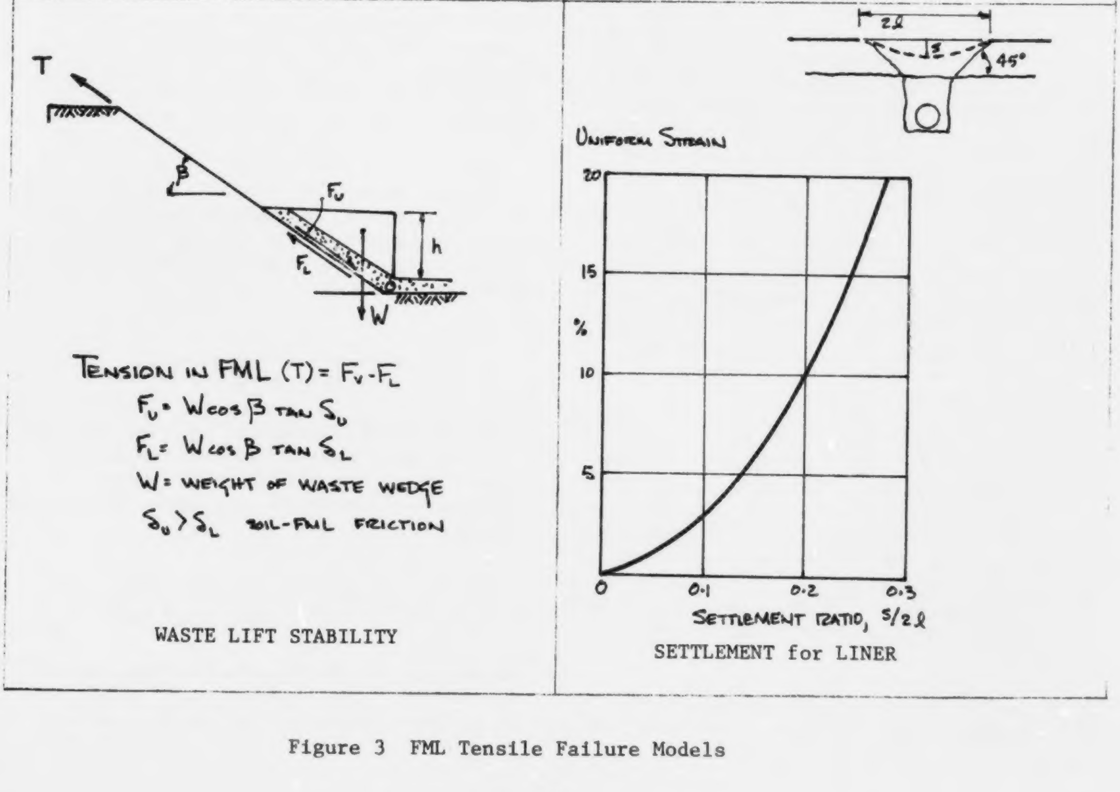
$$T_{tch} = T_{hor} + \frac{(Ka+K')\tan\delta\,[0.5\,\gamma d^2 + qd]}{\cos\beta - \sin\beta\tan\delta} \qquad (2)$$

where d is the depth of embedment, Ka is the active earth pressure coefficient and K' is the at-rest or the passive earth pressure coefficient. The actual anchorage


T
F_L
W sin β
W
β
Tension in FML (T) = W sin β − F_L
W = weight of FML
F_L = soil-FML bond
Stress in FML = T/thickness of FML
F_A
F_U
T
W sin β
F_L
W
β
Tension in FML (T) = F_U − F_L − F_A
F_U = W cos β tan δ_U
F_L = W cos β tan δ_L
F_A = Σ anchor forces above FML
W = weight of layers above FML
δ = FML interface friction

DEAD WEIGHT

SLIDING STABILITY


T
β
F_U
h
F_L
W
Tension in FML (T) = F_V − F_L
F_U = W cos β tan δ_U
F_L = W cos β tan δ_L
W = weight of waste wedge
δ_U > δ_L soil-FML friction
2ℓ
s
45°
Uniform Strain
%
20
15
10
5
0
0.1
0.2
0.3
Settlement ratio, s/2ℓ

WASTE LIFT STABILITY

SETTLEMENT for LINER

Figure 3 FML Tensile Failure Models

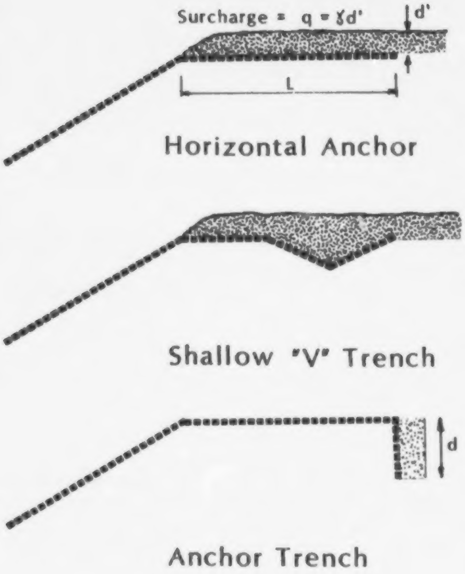


Figure 4 FML Anchorage

capacity lies between that predicted by the two values of K'. The design is then based on the smaller anchorage force to predict DRs based on pullout and the higher anchorage force to calculate stresses in the FML itself.

In service, the FML is also subjected to large normal stresses due to the weight of the overlying waste. These stresses tend to push the FML into the void spaces within the underlying subgrade. Knipshield (4) portrays the stresses acting on a localized portion of the FML as shown on Figure 5. Large subgrade particle size may create void spaces large enough to generate localized failure. While this situation could be minimized by placing a geotextile beneath the FML, this would destroy the intimate contact bewteen the FML and the underlying clay. The limiting normal stress is determined from laboratory tests that simulate the field system described above.

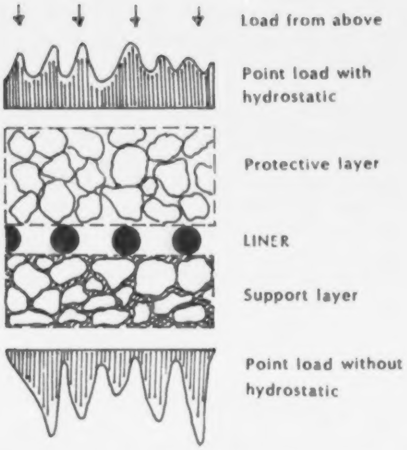


Figure 5 FML Compressive Stresses

DESIGN CONCEPT - LCR

Geosynthetic LCR systems play an important role in the facility by collecting leachate at any location on the liner and conveying it to a low point or sump where it can be removed. The design of the LCR based on in-plane flow is controlled by both the minimun MTG properties and the requirement that no more than 30 cm head of leachate may act on the underlying FML. The head acting on the FML is controlled by the rate at which leachate is being generated and collected within the system, the hydraulic properties of the LCR, and the spacing of the collector pipes within the LCR. These parameters are shown on Figure 6. Early work (5,6) related these parameters to the rate of leachate generation which is commonly not known. The maximum head acting on the FML is then given by

$$H_{max} = \frac{L\sqrt{c}}{2}\left[\frac{\tan^2\alpha}{c} + 1 - \frac{\tan\alpha}{c}\sqrt{\tan^2\alpha + c}\right] \quad (3)$$

where c is defined as the inflow rate divided by the hydraulic conductivity of the LCR. This method has been supplemented by an alternate procedure (7) that is based on the percolation velocity of the leachate. The maximim leachate head using this method is given by

$$H_{max} = \frac{L}{2n}\left[\sqrt{\frac{c}{K} + \tan^2\alpha} \;\; -\tan\alpha\right] \quad (4)$$

where e is the percolation velocity based on conversion of the annual percipitation rate into a uniform velocity (cm/sec).

A synthetic LCR may be composed of a homogeneous material, e.g. a thick nonwoven needled geotextile, or a composite formed of a core that provides planar flow capacity and a surface geotextile that acts as a filter to prevent the adjacent soil from intruding and blocking the core. The planar flow capacity of the LCR is defined by Darcys equation as

$$q = K_p \; i \; A \qquad (5)$$

$$q = K_p \; [dh/L] \; W \; t \qquad (6)$$

where K_p is the permeability in the plane of the LCR, dh is head loss, L is flow length, W is the width of the flow path, and t is the thickness of the LCR. Equation (6) is typically expressed as

$$q = \theta \; [dh/L] \; W \qquad (7)$$

where θ is defined as transmissivity and is equal to the product of K_p and t (8).

The transmissivity of an LCR can be reduced by compression of the core and intrusion of adjacent geotextiles or geomembranes due to soil pressure. These effects can occur elastically as normal loads are increased on the LCR or plastically over time in the completed cell. Laboratory data are shown on Figure 7 for a typical synthetic LCR. These data reflect only the elastic reduction of transmissivity. Long-term tests are rarely performed to evaluate the future reduction in transmissivity due to plastic deformations. Procedures (3) have been presented, however, for estimating these losses based on an analysis of core and filter material creep properties.

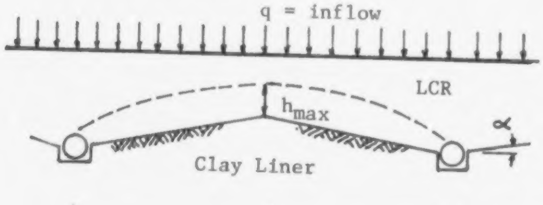


Figure 6 Calculation of Drain Pipe Spacing

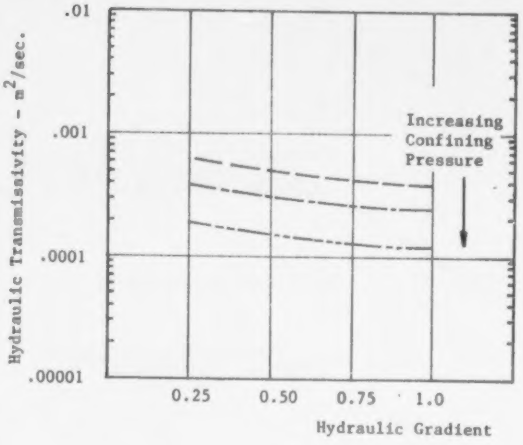


Figure 7 Transmissivity Data
Synthetic LCR

Leachate must first flow through the filter layer of a synthetic LCR before it can be drained away. The filter layer must be selected so that it will filter out the soil particles from the adjacent soil and yet not become clogged by these same soil particles. No true design procedure is at present available to evaluate filtration and clogging potential. There are, however, index tests that indicate the tendency of a given fabric to filter or be clogged by a given soil.

The filtering ability of a fabric has traditionally been related to the Apparent Opening Size (AOS) of the fabric. The AOS is defined as the diameter of glass beads with 5% retained in the fabric after shaking. AOS is appropriate for woven and lightweight fabrics but is questionable for heavy weight nonwoven fabrics. In general, filter criteria guidelines are of the form

$$O_{fabric} = \lambda \; d_{soil} \qquad (8)$$

where O_{fabric} is usually the AOS of the fabric, d_{soil} is a soil particle diameter obtained from a grain size analysis, and λ is an emperical factor. One example of this concept is the filtration criteria by Giroud as presented in Table 1. This method (9) incorporates grainsize data and relative density of the soil. Assuming the fabric manufacturer supplies the AOS for the fabric, the filtration design requires knowledge of fundamental properties of the site-specific soil.

Table 1 Geotextile Filter Criteria (9)

Relative Density,Dr	1<CU<3	CU>3
Loose(Dr<50%)	$O_{95}<(CU)(d_{50})$	$O_{95}<(9d_{50})/CU$
Intermediate (50%<Dr>80%)	$O_{95}<1.5(CU)(d_{50})$	$O_{95}<(13.5d_{50})/CU$
Dense(Dr>80%)	$O_{95}<2(CU)(d_{50})$	$O_{95}<(18d_{50})/CU$

Where Dr is relative density, d_{50} is the grain size corresponding to 50% passing, O_{95} is still equal to the AOS of the geotextile, and CU is the coefficient of uniformity(d_{60}/d_{10}) of the soil.

Clogging of the fabric by soil grains occurs with time. The clogging potential of a given fabric and soil is evaluated in the laboratory using the gradient ratio test or longterm flow tests. The equipment for this test consists of a soil column resting on a geotextile as shown schematically in Figure 8. The test does not reproduce in-situ conditions and as such is only an index test. As water is run through the column, the fabric becomes clogged and a hydrostatic pressure gradient develops across the fabric. If the gradient ratio, as defined on Figure 8, exceeds 3, then there is a potential for clogging of the fabric by the soil. Recent studies (10) have shown that the gradient ratio test may not predict clogging in many critical applications.

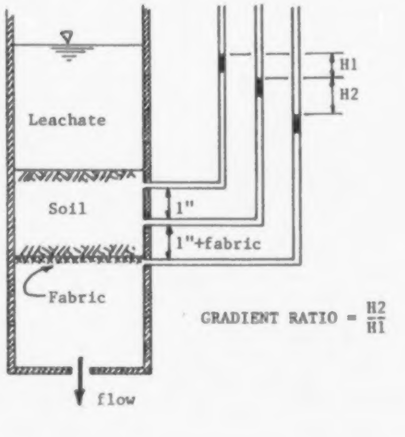


Figure 8 Gradient Ratio Test - Clogging

Long term flow tests use the same apparatus as the gradient ratio test but measure the actual flow rate of leachate passing through the sample over an extended time period. Typical data from a long-term test are shown on Figure 9. The slope of the curve is the focus of attention. If the slope continues to be negative, then the fabric will eventually clog. The combination of an acceptable flow rate and a final slope of zero indicates an acceptable soil/fabric combination.

ADDITIONAL CONSIDERATIONS

Additional geosynthetic components are used in building interior ramps, berms, drainage standpipes, and the cap structure. These ancillary components are not reviewed in this paper.

The designer must also verify that the synthetics used to build the system are resistant to chemical attack from the leachate. While beyond the scope of this paper, guidelines for chemical evaluation are presented elsewhere (11). The designer must also be aware of the need for a better assesment of long-term creep performance of the synthetics, hydraulic problems related to biological growth within an LCR system, and field construction quality control problems. These unknown long-term performance factors and the impact of a failure in these facilities force today's designer to use Design Ratios significantly higher that conventional designs require.

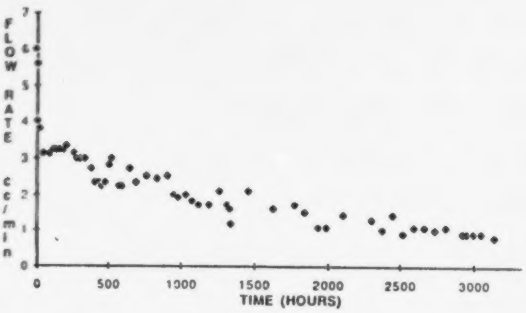


Figure 9 Long Term Flow Test - Clogging

SUMMARY

This paper elaborates on the basic design considerations needed to verify the mechanical and hydraulic performance of the FML and LCR components for double-liner systems for both landfills and surface impoundments. The designs are based on estimates of actual field stress and hydraulic conditions and on laboratory measures of the limit capacities of the synthetic components. These procedures are valid for both short and long-term conditions if appropriate laboratory tests are used.

ACKNOWLEDGEMENT

This work has been sponsored by the U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.

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INSPECTION PROCEDURES/CRITERIA FOR INSTALLATION OF FLEXIBLE MEMBRANE LINERS

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ABSTRACT

Inspection of flexible membrane liner (FML) installation is important in assuring required hazardous waste containment. This paper outlines the procedures and criteria for inspecting the installation of the four most commonly used FMLs for land containment of hazardous wastes:

- Polyvinyl chloride (PVC).
- Chlorosulfonated polyethylene (CSPE).
- High-density polyethylene (HDPE).
- Chlorinated polyethylene (CPE).

The FML installation steps for which inspection procedures are provided include:

- Unloading and storage of FML.
- Preparation and maintenance of the FML supporting surface (earth and other supporting surfaces are discussed).
- Placement of FML on supporting surface.
- FML seaming operations.
- FML anchoring and sealing including anchoring in earth and anchoring to concrete and other materials.
- FML testing including seam testing and testing of the integrity of the entire FML installation.
- FML cover operations.

The FML installer and inspector should be able to follow the guidelines developed by this study in preparing construction quality assurance plans, and in assuring that design plans and specifications are met.

BACKGROUND

FMLs are thin prefabricated polymeric layers of sheets of plastic or rubber commonly used for the containment of hazardous and other wastes. Inspection of an FML installation is important in assuring containment of wastes.

This paper discusses a manual prepared for the EPA which contains the procedures and criteria for inspecting the installation of the four most commonly used FMLs (PVC, CSPE, HDPE, and CPE) for land containment of wastes. The manual is intended for use by regulatory officials, engineering firms, and facility owners/operators. The manual can also be used as a guide in preparing quality assurance plans and as a guide for construction quality assurance inspectors for assuring that design plan and specification requirements are met.

In order to develop a practical document questionnaires were sent to, and interviews were conducted with, manufacturers (raw materials and finished materials), fabricators, lining contractors, testing laboratories, and consulting engineering firms to solicit their comments regarding FML installation. In addition, a thorough review of over 300 documents regarding FML installation was conducted as a further basis for manual preparation.

MANUAL CONTENTS

Discussions among in-house and EPA personnel regarding the presentation format best suited for use by an inspector or other user resulted in the manual being divided into seven chapters that sequentially cover each FML installation procedure. These are:

- On-site unloading/storage of FML.
- Preparation and maintenance of the FML supporting surface.
- Placement of FML on su[illegible]ing surface.
- FML seaming operations.
- FML anchors/attachments.
- FML testing, including seam testing and testing of the integrity of the entire FML installation.
- FML cover operations.

This format allows the inspector the capability of removing chapters individually as he inspects the various installation procedures (assuming the manual is kept in a three ring binder or each chapter is bound separately). It is hoped that the ease of carrying smaller, less cumbersome inspection materials will encourage the inspector to keep the applicable portion of the manual with him as required to assure proper installation.

A brief discussion of each chapter is given below. Copies of the completed manual will be made available through NTIS.

On-Site Unloading/Storage

The initial step of FML inspection is to make sure the specified FML type and accessories are delivered to the job site undamaged. This is primarily the responsibility of the installation supervisor. However, the inspector should also make spot checks.

Once the FML is accepted as undamaged, it is important that it be carefully unloaded onto a surface that is relatively level and smooth, free of rocks, holes and debris to prevent damage to the FML.

FML materials and accessories are best kept out of direct weather conditions to prevent possible damage from sun, wind, or moisture. Quite often the storage area is in the same location as the unloading area. If this is the case, the area must be large enough so that unloading, storage, and transport can operate smoothly. If the storage area is in a building, proper accessibility and maneuverability are of primary importance. A loading dock is also of great value. If the storage area is open it should generally be fenced for security.

Specific sections and subsections in the manual discussing inspection criteria and procedures for on-site unloading/storage are listed below.

- Material check.
  - FML.
  - Accessories.
- Unloading and handling equipment.
- Unloading area:
  - Accessibility.
  - Type.
  - Location.
  - Unloading and handling.
- Storage area:
  - Type.
  - Location.
  - Climatic conditions.
  - Other factors.

Preparation and Maintenance of Supporting Surface

For purposes of the manual, a supporting surface is defined as the surface on which the FML will be placed. For a single FML system, the supporting surface will probably consist of compacted earth, concrete, asphalt, or other material. If a second FML is specified (a double FML system), the supporting surface for the top FML will generally consist of a drainage net, a granular soil layer, and/or a geotextile fabric.

Whether a single or double FML system, it is assumed that the supporting surface has been brought to final grade, and that the earth subgrade (if applicable) has been compacted and is structurally sound.

If the supporting surface is earth, the inspector should be aware that the soil type will effect the installation procedure. For example, clayey soils form surface cracks when dried, and sandy soils form depressions under foot and vehicular traffic. A table containing soil characteristics pertinent to FML installations is included in the manual.

An earth supporting surface should be free of all vegetative growth prior to final preparation. Burrowing animals (e.g., gophers and ground squirrels) should also be removed and/or their tunnels destroyed. Final preparation consists of removing all clods, pebbles, etc., filling in voids, and rolling/compacting the surface.

After the supporting surface has been accepted for FML placement, it is important to maintain its integrity by mitigating or correcting damage caused by wind or storm water erosion, and saturation or ponding by storm water.

Supporting surfaces other than earth (e.g., concrete and asphalt) must also be inspected to assure that they are smooth, free of surface voids or depressions, and that there are no abrupt changes in abutting surface elevations.

The specific sections and subsections as they appear in the manual are as follows:

- Earth supporting surfaces:
  - Type of soil.
  - Vegetation removal.
  - Burrowing animals, ants, and other pests.
  - Preparation of finished earth supporting surface.
  - Maintenance of earth supporting surface.
- Other supporting surfaces:
  - Concrete.
  - Asphaltic supporting surfaces.
  - Geotextile fabric.
  - Drainage layers.

Placement of FML on Supporting Surface

Placement of FML on the supporting surface includes: transporting the FML to the working area; removing the FML from its packaging; and spreading the FML sheets in their appropriate locations, making sure each FML is not damaged (e.g., has no holes, etc.) and is ready for seaming.

Prior to commencing placement of the FML, the inspector should first ensure that placement equipment is on site and in working order; a sufficient number of qualified placement personnel are on site; and weather conditions are suitable.

Specific sections and subsections in the manual discussing placement inspection criteria and procedures are listed below.

- Placement equipment.
- Personnel.
- Weather conditions.
- FML layout:
  - Type of FML.
  - Thickness of FML.
  - Accessibility.
  - Placement on slopes.
  - Placement around penetrations.

Seaming Operations

FML seams can be prepared either in the factory or in the field. Factory seams are manufactured in a controlled environment, and seam quality is generally superior to field seams. Since the field inspector is not responsible for observing the making of factory seams, only a brief summary of factory seaming techniques is provided in the manual as background. However, the overall quality assurance/quality control should require this factory inspection.

The primary objective of the manual is to discuss field seaming operations and the inspection thereof. However, the discussion is necessarily general because each FML manufacturer/fabricator has specific (and often proprietary) seaming equipment and seaming procedures.

Prior to the start of FML seaming operations, the manufacturer should provide the inspector with precise specifications on the equipment and procedures that will be used to seam their material in the factory and field. In addition, the inspector should meet with the manufacturer's/fabricator's representative for an explanation and demonstration of the seaming equipment and procedures to be used on the job.

Seaming methods described include liquid applied solvent or adhesive methods; thermal methods; vulcanizing tapes and adhesives; and tape and mechanical seaming methods.

Specific sections and subsections in manual discussing seaming inspection criteria and procedures are listed below.

- Seaming methods:
  - Factory seams.
  - Field seams.
- Equipment.
- Personnel.
- Environmental conditions.
- Seaming.

Liner Anchors/Attachments

One of the most common sources of failure in an FML installation is the attachment of the FML to another surface. In general, these attachments consist of perimeter anchors or attachments to structures, such as pipes or columns, within the facility.

The manual provides the inspector with guidance on specific types of anchors/attachments, and also delineates several general practices and procedures that should be followed. These include ensuring that placement equipment is on site, in working order, and that a sufficient number of qualified placement personnel are on site.

Specific sections and subsections in the manual discussing liner anchors/attachments inspection criteria and procedures are listed below.

- Placement equipment.
- Personnel.
- Anchors/attachments:
  - Earth anchor trenches.
  - Inspection procedures.
  - Concrete and piping.
  - Concrete.
  - Battens and bolts.
  - Reglets.
  - Piping.

FML Testing

This chapter of the manual introduces the inspector to methods that are used to test factory and field seams and patches. These test methods can be destructive and/or nondestructive. Nondestructive tests are performed in the field on in-place FML. Testing is performed by the contractor and should be observed by the inspector. This type of test retains the integrity of the FML seam or sheet being tested. Destructive tests are performed in either the field or laboratory. The intent is to determine the strength characteristics of a seam sample by stressing the sample until either the seam or the FML sheeting fails. Only tests performed in the field should be observed by the inspector; however the inspector should review laboratory test results to ensure acceptable results were obtained.

Destructive tests can be performed on samples taken from either in-place FML seams, sheets, and patches (destructive sampling), or on samples of representative FML seams and patches fabricated by the seaming/patching crew from the same material, and using the same seaming methods as those being used to make the in-place seams and patches (nondestructive sampling). The inspector should verify that the type of samples used are those specified in the quality assurance/quality control plan.

Field test methods described in the manual are probe, air lance, vacuum box, ultrasonic pulse echo, ultrasonic impedance plane, spark, pressurized dual seam, electrical resistivity, hydrostatic, seam strength peel, and seam strength shear tests. Laboratory test methods described are the bonded seam strength shear and bonded seam strength peel tests.

Specific sections and subsections in the manual discussing FML testing inspection criteria and procedures are listed below.

- Field tests:
    - Air lance.
    - Probe.
    - Vacuum box.
    - Ultrasonic pulse echo.
    - Ultrasonic impedance plane.
    - Spark testing.
    - Pressurized dual seam.
    - Electrical resistivity.
    - Hydrostatic.
    - Seam strength peel.
    - Seam strength shear.
- Laboratory tests:
    - Bonded seam strength, shear.
    - Bonded seam strength, peel.

FML Covers

The primary function of the inspector is to ensure that the FML is not damaged during cover placement operations. Covers over an FML will generally consist of earth (clay [natural and/or bentonite added], sand, silt, gravel, or a combination of soils) or some other material such as portland cement/gunite, geotextile or drainage net.

The majority of the above covers are placed over an FML as a protective layer against mechanical, weather or other potential damage. Drainage nets and sand and gravel are used as a permeable layer to convey leakage and/or leachate that may accumulate on the upper and/or lower FML after being put into use.

Specific sections and subsections in the manual discussing cover type and placement inspection criteria and procedures are as follows:

- Earth covers:
    - Equipment.
    - Personnel.
    - Weather conditions.
    - Earth cover placement.
- Portland cement concrete/gunite:
    - Equipment.
    - Personnel.
    - Weather conditions.
- Drainage nets and geotextiles.

SUMMARY

An improperly installed FML is little better than no liner at all, and may actually be worse, because it provides a false sense of security. Consequently, the role of the inspector in ensuring proper FML installation can be critical. The inspector needs to be aware of all procedures and criteria essential for proper installation, from unloading and storage at the site through actual placement and final cover.

The use of the manual described herein should play a major role in standardizing inspection procedures and in ensuring proper installation of FMLs at hazardous waste sites.

AN ASSESSMENT OF MATERIALS THAT INTERFERE WITH STABILIZATION/SOLIDIFICATION PROCESSES

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ABSTRACT

Stabilization/solidification of hazardous waste involves mixing the waste with a binder material to enhance the physical properties of the waste and to immobilize contaminants that may be detrimental to the environment. Many hazardous wastes contain materials that are known to inhibit the setting and strength development properties of commonly used stabilization/solidification binder materials. This paper describes the initial results of an evaluation into the affect of ten interfering agents: oil, grease, lead nitrate, copper nitrate, zinc nitrate, sodium hydroxide, sodium sulfite, phenol, trichloroethylene, and hexachlorobenzene on the setting and strength development properties of a metal hydroxide sludge stabilized/solidified with three binder materials (Portland cement, lime/flyash, and cement/flyash).

The setting and strength development properties of the waste-binder-interfering agent mixture were evaluated using the unconfined compressive strength (UCS) test. UCS data indicated that relatively low levels (less than 8 percent) of phenols, lead nitrate, oil, and grease can result in an 80 percent reduction in the 28-day UCS developed by the waste-binder-interfering agent mixture as compared to control specimens. Trichloroethylene and hexachlorobenzene where shown to have little effect on strength development.

The results of this research confirm the need for waste-binder specific studies prior to the selection of a chemical stabilization/solidification process for the treatment of hazardous wastes.

INTRODUCTION

Background

The Environmental Protection Agency (USEPA) is responsible for evaluating the suitability of hazardous waste and materials for land disposal. Chemical stabilization/solidification (S/S) is one technique that has been proposed as a means of controlling the release of contaminants from landfilled wastes to surface and ground waters. Indeed, S/S of hazardous wastes is recognized in regulations implementing both the Superfund Amendments and Reauthorization Act of 1986 (SARA) and the Hazardous and Solid Waste Act Amendments of 1984 (RCRA).

A variety of S/S technologies have been proposed for treating hazardous wastes. The most commonly applied technologies use cement, pozzolan, or cement-pozzolan combinations as the primary means of contaminant immobilization (U. S. EPA 1980, Cullinane et al. 1986). A potential problem with using S/S technology involves chemical interferences with the hydration reactions typical of the cement and pozzolan processes. Experience in the cement and construction industry has demonstrated that small amounts of some chemicals can significantly affect the setting and strength development characteristics of concrete. Consequently, the cement industry has developed fairly stringent criteria for the quality of cement, aggregate, water, and additives (accelerators or retarders) that are allowed in concrete (Jones et al. 1986).

Of particular concern to S/S technology is the affect of organic compounds on the strength and contaminant immobilization characteristics of the final product. It is well documented that small concentrations of organic compounds (Young 1972, Young 1973), sugars (Ashworth 1965) formaldehydes (Rosskopf 1975) and various chemical contaminants typically found in hazardous waste affect the setting mechanisms of pozzolan cements and lime flyash pozzolans. Roberts (1978) and Smith (1979) reported on the affects of methanol, xylene, benzene, adipic acid, and an oil and grease mixture on the strength and leaching characteristics of a typical lime/flyash S/S formulation. Smith (1979) concludes that there was a good correlation between the effects of organic compounds on lime/flyash pozzolanic systems and the reported effects on the hydration of Portland cement. More recently, Chalasani, et al. (1986) and Walsh, et al. (1986), using x-ray diffraction and scanning electron microscopy techniques, reported on the affects of ethylene glycol and p-bromophenol on the microstructure of Portland cement hydration products. Ethylene glycol was found to produce significant changes in the microstructure up to at least a year of curing time.

Purpose and Scope

The purpose of the research described by this paper is to develop data on the compatibility of ten waste constituents with three binding agents - Portland cement, Portland cement/flyash, and lime/flyash pozzolan cement. Only the results of the unconfined compressive strength (UCS) test are presented in this paper. The remainder of the data will be presented in a comprehensive report scheduled for publication in 1988, after completion of the project.

MATERIALS AND METHODS

Jones et al. (1985) described the basic research program to evaluate the effects of interfering compounds on S/S processes at a previous conference. The study reported on herein was conducted in three phases: (1) preparation of a synthetic wastewater and sludge; (2) addition of a binder and interfering material to the sludge; and (3) UCS testing of cured specimens containing sludge, binder, and interference chemicals.

Synthetic Wastewater and Sludge Production

Initial laboratory tests revealed that a synthetic wastewater containing nitrate salts of cadmium, chromium, nickel, and mercury at 600 times the EPA extraction procedure limit could be treated with calcium hydroxide to produce a hydroxide sludge with typical metal concentrations of 86.2, 84.1, 18.8, and 0.137 mg/g (dry weight basis) of nickel, chromium, cadmium, and mercury respectively.

Typically, the raw sludge contained 8 percent solids and was very fluid. The sludge was dewatered to approximately 30 percent solids using a rotary drum vacuum filter. A constant moisture content between sludge batches was maintained by adjusting the solids content of the dewatered sludge to 25 percent using the supernatant liquid from the sludge production process as a dilution liquid.

Specimen Preparation

The 25 percent solids content sludge was divided into three 150 gallon samples and binder material was added to each at the following ratios.

Binder	Binder/Sludge Ratio
Portland Cement (Type I)	0.3:1 Cement:Sludge
Portland Cement (Type I)/Flyash (Type F)	0.2:1 Cement:Sludge 0.5:1 Flyash:Sludge
Lime/Flyash (Type C)	0.3:1 Lime:Sludge 0.5:1 Flyash:Sludge

After mixing the sludge with the binder, each binder/sludge sample was subdivided into four equal parts. One of the ten interfering chemicals was added to each of the subsamples at ratios of 0, 0.02, 0.05, and 0.08 (by weight) interference chemical to binder/sludge material. The subsample to which no interference chemical was added was used as a control specimen. A control specimen was prepared each time an interference chemical was processed, thus accounting for variability between batches, so that the UCS results between batches could be compared.

The interference/binder/sludge mixture (I/B/S) was then molded into two inch cubes in accordance with ASTM Method C-109-77/86 (ASTM 1986). Because the I/B/S mixture was usually viscous and could not be tamped into the molds, the ASTM method was modified to include vibration of the I/B/S mixture to remove any air pockets that developed during the molding process.

The specimens were cured in the molds at 23° C and 98 percent relative humidity for a minimum of 24 hours and removed from the molds whenever they developed sufficient strength to be free standing. After removal from the molds, the specimens were cured under the same conditions for periods of 4, 11, and 28 days. At the end of each curing period, the UCS of the specimens was determined in accordance with ASTM C 109-77/86.

DISCUSSION OF RESULTS

Space limitations do not allow presentation of all the study results. Typical results for selected interferences are discussed below.

Table 1 presents the results, reported as the percent increase or decrease in 28-day UCS from the control specimen. Figures 1 through 5 present a graphical representation of the results of the study. Figure 1 presents the UCS versus curing time for the cement binder-sodium hydroxide interference. Each curve represents the strength development curve for one interference concentration. Figure 2 presents the 28-day UCS versus interference concentration for each of the three binders for the sodium hydroxide. Figures 3, 4, and 5 present a graphical representation of the relative effects of interference concentration on the 28-day UCS of the three binders.

The data for the 28 day UCS are an indicator of the UCS trends observed at the earlier curing periods. This is clearly illustrated in Figure 1 which is a plot of cure time versus UCS for one interference material. Although the slope of the curves varies between binder and interference treatments, in most cases, the lines of constant interference concentration do not cross.

Portland Cement Binder

The data presented in Table 1 clearly indicate that the interference effects may be positive or negative, depending on the concentration of the interfering material. The addition of oil or grease at a 0.08 ratio resulted in a 44 percent decrease in the 28-day UCS. The addition of copper nitrate, resulted in an increase in UCS for all concentrations. The addition of copper nitrate at a 0.05 ratio resulted in a 181 percent increase in the 28-day UCS. The addition of zinc nitrate resulted in the an increase in UCS for the 0.02 ratio; however, when added at a 0.08 ratio, it resulted in the largest UCS decrease, 85.5 percent, observed for any of the interference compounds. For cement, most specimens exhibited a decrease in UCS with increasing interference concentration.

By comparing the UCS results for the control specimens for different binders, it is evident that the cement specimens developed less strength than the lime/flyash or the cement/flyash specimens. Figure 2 however illustrates that increasing the concentrations of the interference chemical does not necessarily affect the different binders to the same degree.

Portland Cement/Flyash

The addition of a 0.08 ratio of lead nitrate, copper nitrate, zinc nitrate, and phenol resulted over a 90 percent decrease in 28-day UCS. The effect of sodium hydroxide, sodium sulfate, and copper nitrate addition was interesting because of the increase in UCS at the lower concentrations and decreases in UCS at the higher concentrations. The addition of a 0.02 ratio of sodium hydroxide resulted in a 22.8 percent increase in 28-day UCS while the addition of a 0.08 ratio caused a 19.5 percent decrease in 28-day UCS. The effect of hexachlorobenzene was not concentration dependent and resulted in a consistent 9 percent decrease in 28-day UCS, regardless of concentration.

Lime/Flyash

The addition of a 0.08 ratio of lead nitrate, copper nitrate, zinc nitrate, sodium sulfate, and phenol resulted in an 80 percent decrease in 28-day UCS. The addition of trichloroethlene, hexachlorobenzene, sodium hydroxide, and sodium sulfate resulted in a gain in 28-day UCS (51.0, 6.2, 71.1, 65.2 percent respectively) at the 0.02 ratio; however, these same compounds resulted in a decrease in strength (34.4, 1.2, 3.6, and 81.8 percent respectively) at a 0.08 ratio. The addition of oil or grease at a 0.08 ratio resulted in a 32 and 54 percent decrease respectively, in 28- day UCS.

CONCLUSIONS

Several conclusions can be drawn that characterize the effects of the interference materials investigated in this project on the UCS of stabilized/solidified waste materials.

1. The interference chemicals tested had a measurable effect on the setting and strength development properties of the stabilized/solidified waste. The magnitude of the effect depended on the type of binder, the curing time, and the type and concentration of the interfering compound.

2. Stabilized/solidified waste will show decreases in UCS development with increasing oil or grease concentrations.

3. Although the waste stabilized with Portland cement resulted in lower 28-day strength development, it appears that the concentration of interference material had less of an effect on the UCS development properties for the Portland cement binder than for the Portland cement/flyash or lime/flyash binders.

4. Zinc and phenol concentrations above 5 percent resulted in marked decreases in 28-day UCS development for all the binders tested.

5. Sodium hydroxide tends to increase the UCS at lower concentrations and decreases the UCS at higher concentrations for all binders.

6. The chlorinated hydrocarbons evaluated in this study had little effect on the UCS development properties.

ACKNOWLEDGEMENTS

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TABLE 1. 28-DAY UNCONFINED COMPRESSIVE STRENGTH AS A PERCENT OF CONTROL SPECIMEN[1]

Interference	Portland Cement Binder I/B/S[2] Ratio			Cement/Flyash I/B/S Ratio			Lime/Flyash I/B/S Ratio		
Chemical	0.02	0.05	0.08	0.02	0.05	0.08	0.02	0.05	0.08
Oil	-20	-38	-44	-8	-28	-42	-7	-27	-32
Grease	-12	-25	-45	-48	-40	-20	-7	-27	-54
Lead Nitrate	- 2	+18	+10	-51	-75	-97	-40	-77	-90
Copper Nitrate	+91	+181	+4	+17	-84	-98	-48	-48	-98
Zinc Nitrate	+3	-73	-86	-47	-93	-95	-53	-77	-88
Trichloroethylene	-28	-36	-27	-7	-33	-29	+51	-20	-34
Hexachlorobenzene	-5	-6	+15	-10	-9	-10	+6	+9	-1
Sodium Hydroxide	+14	-33	-52	+23	+5	-20	+1	-7	-4
Sodium Sulfate	-7	-13	-53	+23	+16	-64	+65	+38	-82
Phenol	-22	-26	-54	-49	-82	-92	-65	-88	-96

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[1] All results reported as percent increase (+) or decrease from the control specimen rounded to nearest whole percent.

[2] Interference to binder/sludge ratio.

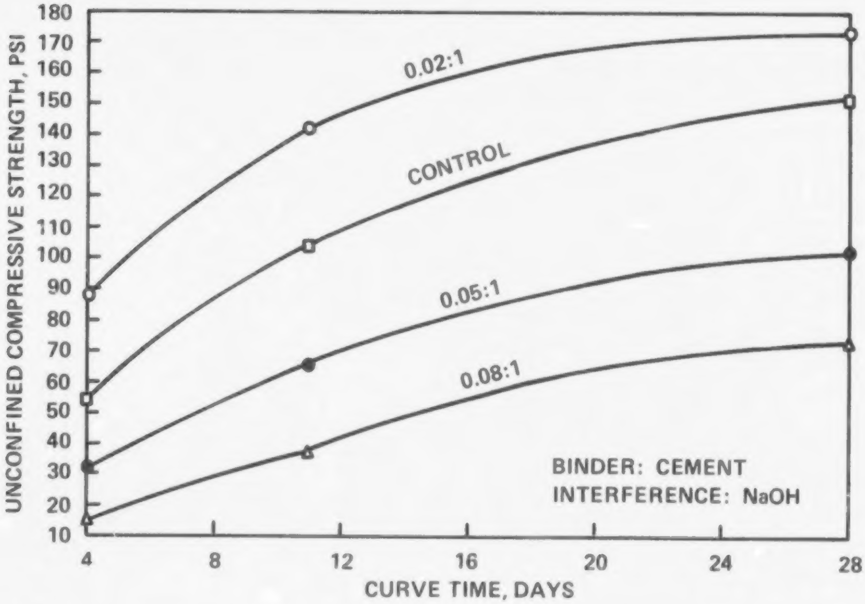

Figure 1. Unconfined Compressive Strength as a Function of Curing Time and Interference Concentration

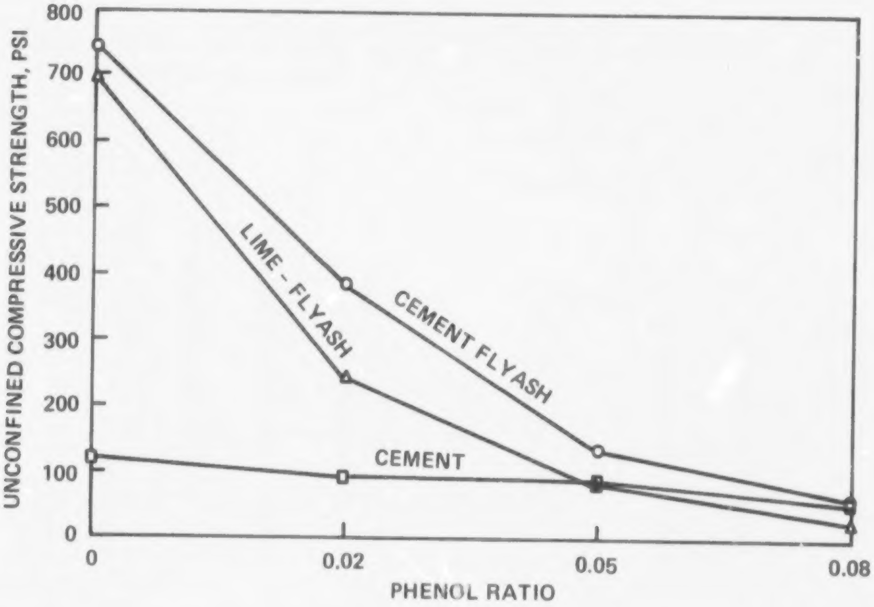

Figure 2. Unconfined Compressive Strength for Three Binders as a Function of Interference Concentration

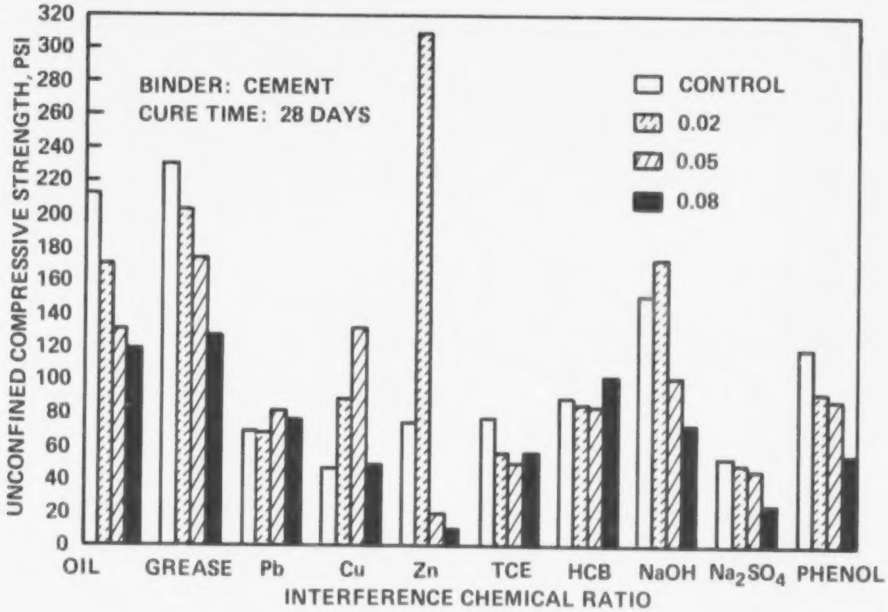

Figure 3. Effect of Interference Concentration on 28-day UCS for Type I Portland Cement Binder

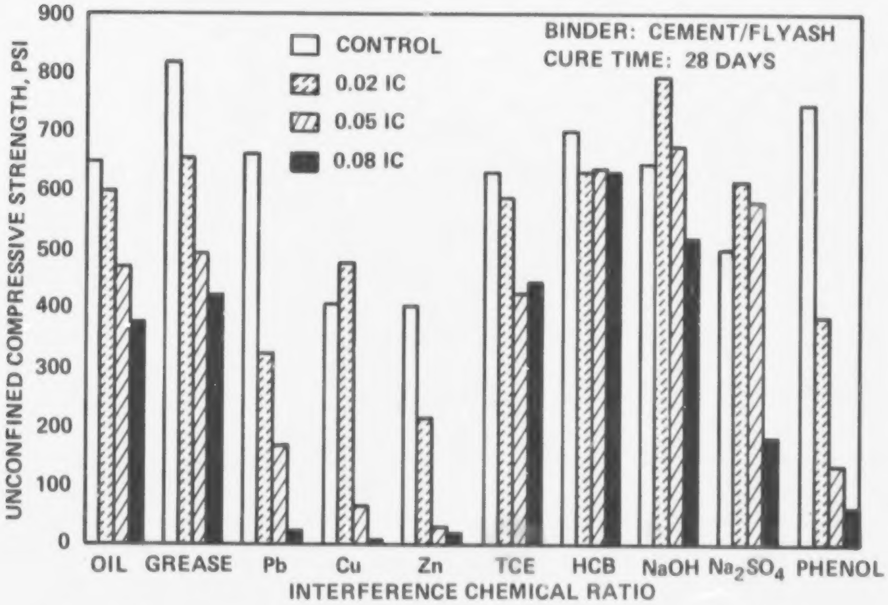

Figure 4. Effect of Interference Concentration on 28-day UCS for Cement/Flyash Binder.

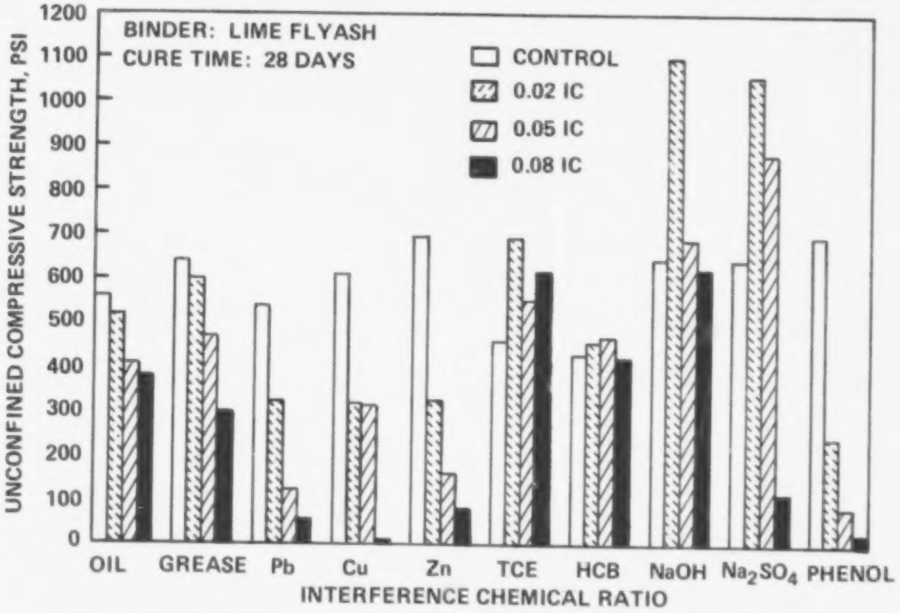

Figure 5. Effect of Interference Concentration on 28-day UCS for Lime/Flyash Binder.

MINE WASTE/OVERBURDEN ANALYTICAL TECHNIQUES - CHARACTERIZATION AND SIMULATION OF MINE TAILINGS WEATHERING ENVIRONMENTS

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ABSTRACT

The prediction of mine drainage quality is based on the chemical weathering attributes of the mine waste/overburden that is produced by the mining operation. These are generally assessed through overburden analyses, which fall into two broad categories, static or dynamic techniques. In the static tests, drainage quality projections are based on whole rock analyses. Alternatively, dynamic tests subject the samples to simulated weathering tests and monitor the quality of the effluent produced. Within these two categories several mine waste/overburden analytical techniques are available, each having advantages and disadvantages relative to the other. An extensive computer literature search identified the most popular analytical techniques and includedcolumn leaching tests, humidified cells, soxhlet reactors, BCR initial and confirmed (bacteria) tests, and acid/base accounting. These analytical procedures were further structured to evaluate the effect of alkaline pore water, air lock, and interstitial sulfide reactivity.

In a preliminary study, several mine waste/overburden analytical techniques were evaluated to determine which one most closely approximates observed field conditions. Fractions of an acid producing pyrite rich ore found at a gold mine in South Carolina were contained in plastic tubs and exposed to the atmosphere. The volume and quality of the leachate produced after each rain event were related to the weight of the sample. These field derived data provide the background against which the laboratory analyses of splits of the samples were compared and evaluated.

In the preliminary test, we found the finer the particle size, as prescribed by the particular test, the greater the amount of acidity produced. In essence, the acid production potential is an artifact of the particular test used and, to a lesser degree, the chemistry of the sample.

INTRODUCTION

Acid drainage is a problem common to operations that expose metallic disulfides (most commonly pyrite and marcasite) to atmospheric conditions and oxidizing environments. In the process a highly acidic, sulfate-iron enriched solution is generated that may severely impact the environment.

The evaluation of the acid production potential of a sample is based on the accurate assessment of the sample's chemical weathering attributes. These assessments are generally performed through mine waste/overburden analyses, which can be grouped into two broad categories, static or dynamic techniques. In the static tests, whole rock analyses are used to predict mine drainage quality; the assumption being the specific minerals comprising the mine waste/overburden will react with water to produce varying degrees of alkalinity and acidity (the projected concentrations of which are balanced to determine the character of the drainage). Alternatively, dynamic tests empirically determine leachate quality by subjecting the samples to simulated weathering conditions while monitoring the quality of the effluent produced. Within these two categories a variety of mine waste/overburden analytical techniques is available, each having advantages and disadvantages relative to the other.

Through a computer literature search, examining 679 titles and 36 abstracts dealing with various aspects of mine drainage quality and predictive methods, we identified several mine waste/overburden analytical techniques widely used in the United States and Canada, both in the coal fields and sulfide mines. These methods include simulated weathering chamber tests (column and humidity cells), soxhlet reactors (infrequently used), biological confirmation tests (commonly referred to as B.C. Bacterial test), and whole rock analyses (acid/base accounting, extensively used in coal fields), and B.C. Research Initial test (extensively used for base metal and gold mines in Canada and western U.S.). The test involving the peroxide oxidation of the sample has been recently published and lacks widespread usage. The various tests are summarized and described in Table 1.

Many questions exist as to the accuracy of the testing procedures and the ability of the tests to adequately project the long-term (decades) chemical weathering attributes of mine waste/overburden material based on laboratory results obtained in relatively short time periods (days to weeks). In addition, the variety of environmental conditions relative to climate, mining operation, enrichment or recovering processing methods and manner of disposal, have a mitigating effect on the oxidation of the sulfide and manner by which the weathering products are mobilized from the site. For example, the acid potential of some tailings will be greatly affected by the manner of disposal. Consider the fine grained particle size of the tailings material which will afford the sample with a large water holding capacity (specific retention) and create an "air lock" that will effectively inhibit the transfer of oxygen required for pyrite oxidation and restrict the oxidation zone to the near surface meter of the disposal site.

The fact that many of the tailings piles are located in areas where the evapotranspiration exceeds precipitation, requires that the analytical results obtained from dynamic tests be reexamined in the context of non-leaching environments. Assuming oxidation of the sulfide mineral to take place, the dissolution and mobility of the acid producing weathering products is precluded by the lack of internal drainage.

Further, some of the processing plants utilize slaked lime to enhance recovery of the ore and in the procedure render the discharge water/tailings mixture alkaline. Other than the inhibitory effect that the alkalinity has on pyrite oxidation, the alkalinity of the pore water may have a substantial neutralization potential and effectively neutralize any acidity produced.

Thus, other than the intrinsic chemical nature of the tailings material, the environmental factors that may play a role in the overall weathering process and affect the sample's acid production potential, must be included as part of the assessment.

The objectives of this study are 1) to determine which of the variety of mine waste/overburden analytical techniques methods most closely approximate field conditions and 2) to evaluate the effects of porewater chemistry, "air lock" potential and leaching interval (frequency) on acid production potential.

METHODS

The study was divided into two parts, one dealing with the intrinsic nature of the analytical procedures, normalizing the environmental effects and utilizing a pyrite rich ore from a gold mine in South Carolina. The second part deals with an evaluation of the environmental effects using selected analytical procedures and mine tailings from several copper mines in the West.

We report on the results of the first part of this study, evaluating the analytical procedures, and describe the strategy of the second part of the study that was initiated during the Spring of 1987, and for which preliminary results will be presented during the Symposium.

First Part of the Study

Samples for this study were collected from a gold mine in South Carolina. Idle for about 40 years, this site was mined initially for gold and subsequently for pyrite. Acidic waters drain from a large acid lake and small, highly acidic seeps emanate from the talus and gangue heaps.

For the first part of this study, various size fractions of an acid producing pyrite rich ore were contained in plastic tubs (approximately 0.5 m x 0.5 m x 0.3 m deep) and exposed to rainfall. Representative splits from each were collected for simulated weathering tests and whole rock analysis. The leachate generated

TABLE 1. SUMMARY OF MINE WASTE/OVERBURDEN ANALYTICAL TECHNIQUES COMMONLY USED IN THE UNITED STATES AND CANADA

Static Tests	Method	Advantages	Disadvantages
Whole Rock Analyses			
• Acid/Base Accounting (1)	Whole rock analyses completed on a pulverized sample. Acid potential related to sulfur content, neutralization potential determined by hot acid digestion with HCl.	Easy to perform, quick turn-around time, useful in areas that are acid or alkaline prone.	Does not relate to kinetic data. Assumes parallel release of acidity and alkalinity which provides inaccurate results.
• British Columbia Research (BCR) test (2)	Whole rock analysis completed on pulverized sample. Acid potential related to sulfur content, neutralization capacity obtained by titration with H_2SO_4.	Same as above	Same as above
Dynamic Tests			
• Soxhlet Reactor (3)	Leachate generated on pulverized sample which is cycled in a soxhlet reactor. During interim, sample is allowed to dry at 105° C.	Easy to perform quick turn-around time, purported kinetic data.	Expensive apparatus, extremely aggressive oxidation of sample which is not related to any natural process.
Simulated Weathering Tests			
• Humidity cells (4)	Crushed rock is placed in humidified atmosphere and leached periodically. Volume and character of leachate related to rock weight to produce alkaline/acid production potential.	Produces kinetic data, rates of acidity per unit weight of sample obtained, approximates field conditions.	Long time required, large data base generated.

• Column Weathering test (5)	Field sample placed in large columns and and leached periodically. Leachate is analyzed and related to rock weight.	Best approximator of field conditions.	Same as above, in addition large volume of samples required, channelization problem encountered.
• Beaker Leachate test (1)	Pulverized sample is placed in water and chemistry monitored through time.	Simulates submerged conditions of mine waste, some kinetic data.	Does not allow for easy transfer of oxygen which may be rate limiting.
• BCR Bacteria test (6)	Pulverized sample is oxidized in presence of bacteria. pH monitored through time, sample continuously shaken.	Easy to use, incorporates bacteria in reactions.	Data identify sample as acid producing; results cannot be correlated or related to kinetic test data.
• Peroxide test (7)	Pulverized sample is oxidized in the presence of hydrogen peroxide and rate of pH change monitored through time.	May be completed in field, very rapid results.	Sample pH response is to be calibrated against larger sample to translate data to field conditions; indirect testing of alkaline samples.

is collected and analyzed for volume, pH, specific conductance, acidity, and sulfate. In turn, these data are converted to milligrams of acid produced per kilogram of sample and provides the basis against which the results of the laboratory overburden analyses are compared and evaluated.

Field Tub-Control Samples

The tests performed to date utilized three different sized populations (2.5 cm or small-S, 2.5-5 cm or medium-M, and 7-10 cm or large-L) selected from the pyrite rich ore found at the site.

The plastic tubs, containing known sample weights, were placed in an open field, one meter above the ground. Following a rain event, the amount of rainfall (cm) and the volume of effluent (liters) produced by the tubs (which drain into sealed plastic barrels placed beneath the tubs) were recorded. An aliquot of effluent was collected and analyzed within 24 hours for specific conductance, pH (hot and cold), acidity, and sulfate.

The analyses, expressed as concentrations 1 (mg/l), are converted to loads (mg) of component produced by multiplying the concentrations by volume of the effluent. In turn, these loads may be normalized for particular sample weights to a kg base and percentage sulfur. Plotted versus time, cumulative acid loads produced per kg of sample, yield rates of acid produced against which the laboratory analyses are being compared and evaluated.

Column Leaching

Samples of known weight and size were placed in plexiglass columns of 9 cm diameter and 30 cm length. Column S contained 3090 g of sample S and filled the column to approximately 4/5 its length (23 cm). Column M contained 2181 g of sample M and filled the column to a height of 18 cm. Column L contained 2089 g of sample L, filled to a height of 17 cm. Each column drained into a 1000 ml sample bottle. The top of each column was sealed with plastic-wrap to prevent contamination and to maintain humid conditions between leachings.

The columns were leached every seven days by spraying the top of the column with 500 ml of deionized water and allowed to drain for 12 hours. The leachate collected was analyzed for specific conductance, pH (hot and cold), acidity, and sulfate concentrations.

Humidity Cell Weathering Tests

Samples of known weight (approximately 200 grams (g)) and crushed to pass 4 millimeters (mm) were placed onto a filter paper in separate chambers. Duplicate humidity cells chambers were constructed for each sample size (S, M, L), for a total of six chambers. The chamber was a plastic cylindrical pan, 7 cm deep and 15.5 cm in diameter. A plastic lid prevented contamination and evaporation. Humidified air, generated by bubbling air through water in a closed aquarium, is circulated into the chamber to maintain saturated conditions. The chamber is opened only to add water during the leaching cycle.

Samples were leached every seven days by slowly pouring 100 ml of deionized water onto the sample and stirring for one minute. Following, the lid was replaced and the water - rock mixture was drained through a basal outlet into a graduated cylinder for 12 hours. The leachate collected was analyzed for specific conductance, pH (hot and cold), acidity, and sulfate.

Soxhlet Extractors

Pulverized (to pass 125μ) samples of known weight were placed in separate cellulose extraction thimbles and stored in a drying oven at 100° C. Every seven days the samples (in thimble) were placed in separate soxhlet reactors and 250 ml of deionized water was circulated through the sample for 4 hours. The heat source was a GLAS-COL heating mantle (run at 120 volts). After 4 hours, the heating mantle was turned off and the soxhlet reactor allowed to cool to room temperature. The leached sample was returned to the drying oven and stored at 100° C in preparation for the next leaching cycle. The effluent collected in the soxhlet was analyzed for specific conductance, pH (hot and cold), acidity, and sulfate.

B.C.R.

This test was run in triplicate, three equal weight pulverized (to pass 125μ) portions of each sample (S, M, L) were weighed out and each placed in separate 300 ml Erlenmeyer flasks to which were added 70 ml of 9K medium (8). Sufficient sulfuric acid was added, if necessary, to bring the initial pH to 2.5. The flasks were continuously shaken for 4 hours to homogenize the sample and medium, and innoculated with 5 ml of viable Thiobacillus ferrooxidans culture. The pH was monitored every day for the first three days and every other day thereafter. This was continued until the pH readings maintained a constant value (indicating cessation of microbiological activity) or until the pH dropped to 1.8. At this point, half of the weight of the original sample was added and the sample agitated for 24 hours. If the pH was then greater than 3.5 the test indicates the samples to be non-acid. Otherwise, an additional sample portion (again half the weight of the sample) is added and the sample agitated for 24 hours. At this point the pH was either greater than 4.0 or less than 3.5 (the sample is an acid producer), the test was to be terminated. Samples with pH falling between 3.5 and 4.0 were to be shaken for 48 hours and a final pH recorded (9).

The shaker table and sample flasks were housed within a plastic chamber that trapped the heat generated by the operating shaker table and maintained conducive to bacterial activity (30-35° C).

RESULTS

The results of the tests are presented for the first 70-80 days of the study. With the exception of the acid/base accounting data and the B.C.R. Bacteria test results, all leachate data have been adjusted and normalized to cumulative mg of acid produced per 1 kg of sample. These acid production trends are shown in Figures 1-7 and summarized in Table 2. The laboratory analyses of the samples spanned an 82 day time period; the data presented in Table 2 are for an 80 day interval.

For control tubs, humidified cells, and column tests the time scale (x-axis) is in days. The soxhlet samples were leached weekly for four hours at a time, and accordingly, the time scale for the soxhlet experiment is in hours.

The tub-field data (Fig. 1) show a nearly identical behavior between samples L and S. Sample M exhibited more than double the cumulative acidity of S and L throughout much of the 80 day period. All three curves show a pronounced decline in acid production for the last two weeks of this period.

The results of the column tests most closely parallel those in the field, in terms of both cumulative acidities and intersample variation (Fig. 2). The increases in cumulative acidity were more

TABLE 2. NORMALIZED CUMULATIVE ACIDITIES FOR VARIOUS ANALYTICAL TECHNIQUES

Sample Analyses	Cumulative Acidity (mg/kg/80 days)
Control (Tub)	250 - 750
Column Test	300 - 695
Humidity Cell	1,600 - 2,100
Soxhlet	11,000 - 15,500 mg/kg PER 50 HOURS

linear for the column tests than for those in the field. This is an artifact of the constant periodicity and leaching volumes which were controlled in the laboratory tests.

The simulated weathering chamber tests demonstrated much less inter-sample variation, though the two M samples had higher cumulative acidities towards the end of the 80 day leaching period (Fig. 3). The humidity cell tests clearly over-predicted the cumulative acidity found in the field.

The results of the soxhlet tests exhibit a different inter-sample variation than those of the other lab and field results. While sample M greatly outproduces sample S, both duplicate L samples attain greater cumulative acidities than M towards the end of the period. Cumulative acidities for the soxhlet extractors are an order of magnitude greater than those found in the field (Fig. 4).

DISCUSSION

Of the simulated weathering tests it appears that the column tests more closely approximate the quality of the leachate derived under natural conditions. The humidity cell overestimates the amount of acidity, while the soxhlet greatly overestimates the acidity. The observed variations in acid production occurring between the control and humidity cell are explained by differences in grain size (the humidity cell sample utilizes sample sizes of 2-4 mm). The soxhlet utilizes pulverized samples (125μ) and, in addition, subjects the samples to 105° C drying temperatures at weekly intervals, generating skewed and exaggerated results.

The whole rock analyses tests (B.C.R. initial and Acid/Base Accounting) indicated potentially acidic samples. Because the samples used in this study are pyrite-enriched - calcareous material deficient, we should not expect otherwise.

The B.C.R. bacteria tests, in essence, also confirmed the samples to be acid. In all sets of tests, the pH was reduced from 2.6 to 1.7 in 4 to 17 days (Figures 5-7). The biological confirmation test results are difficult to interpret in either a quantitative or comparative manner. The data generated are pH (the test parameter) versus time (days) and the results indicate the variability between triplicates of a particular sample to be as great as that found between samples.

For the B.C.R. tests the parameter monitored is pH and at the levels measured for these tests the system is buffered. Accordingly, there is no indication of the amount of acid produced, and the B.C.R. test data (which monitors pH) cannot be compared to acid production rates (measured by titration with a standard base). The test, in its present form, is primarily qualitative in nature.

In summary, for the tub, column, and humidified cell tests, it appears that the acid production potential derived from a particular overburden analytical technique is more a function of the sample size required to perform the particular test than the chemistry of the sample. In the soxhlet tests further comminution of the sample, coupled with an unnatural aggressive oxidizing environment, produces orders of magnitude more acid than the other leaching tests. All things considered, the column tests more closely approximate the observed field results than the other analytical tests.

SECOND PHASE OF THE STUDY

The analytical techniques used in this study can also be used to evaluate the various environmental factors affecting leachate quality. Using copper mine tailings as the test sample, heavy liquid separation methods are used to concentrate the heavy mineral fraction (which includes the sulfides and is the acid producing component). In turn, the heavy fraction is rinsed with acetone and deionized water and analyzed with the soxhlet reactors.

Inasmuch as the tailings will not be crushed further, the variability in acid production by sample size is eliminated. Thus, the acid producing component of the sample can be evaluated.

Using the weathering chambers, tailings samples as received and rinsed with deionized water, can be tested to evaluate the effect that pore water chemistry and matrix mineralogy have on the tailings' potential to produce acid. This will simulate the conditions expected to occur at the near surface environment of tailings ponds. In addition to a humidified air environment, the test may also be structured to simulate oxidation processes occurring under semi-arid conditions and in the presence of ultra-violet light.

To test the effect of "air lock" as might occur at depth within the tailings ponds, the column tests can be used with rinsed and un-rinsed samples. The leachate qualities derived from the columns and weathering chambers can be compared to evaluate the magnitude of the environmental factors as thought to occur near surface and at depth within tailings ponds.

Finally, the leaching interval is controlled and the mass tranfer of water documented (i.e. volume of water added and leachate volume are recorded), which, in turn, can be related to the mass transfer of water through a tailings pond in response to various climatic conditions. Given an evaporation loss, precipitation rate and effective porosity, pore volume displacements can be calculated and related to geochemical mobilities within the pond body.

This phase of the study is currently underway and preliminary results should be available for presentation at the Symposium.

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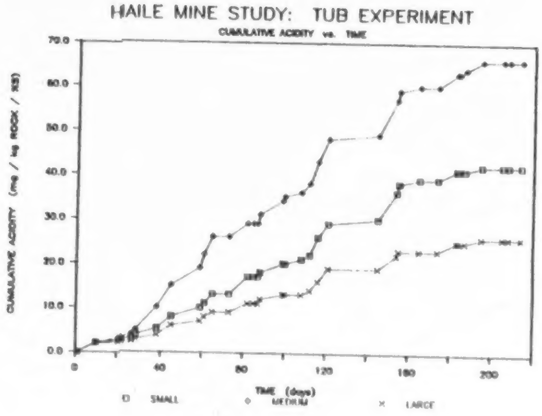
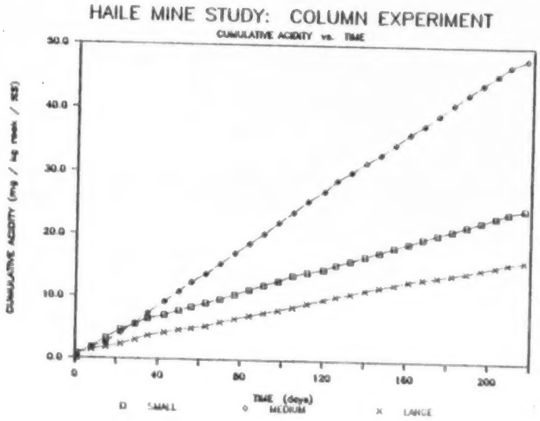


Figure 1



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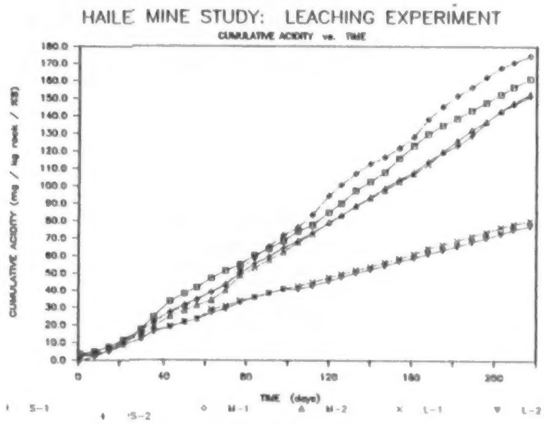


Figure 3

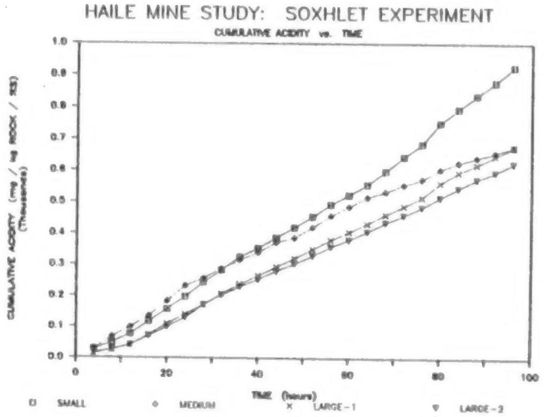
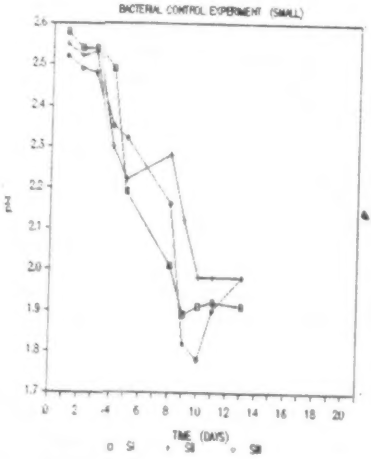
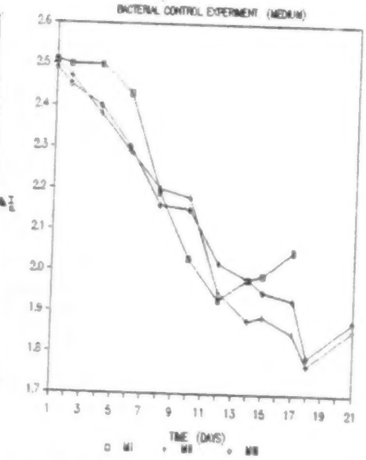


Figure 4





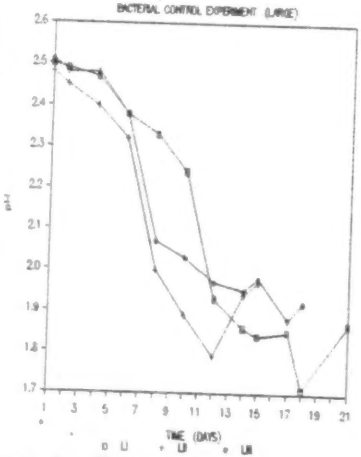


Figure 5- pH vs Time (S) Figure 6-pH vs Time (M) Figure 7- pH vs Time (L)

THE EFFECTS OF OVERBURDEN PRESSURE AND HYDRAULIC GRADIENT ON THE PERFORMANCE OF MODEL SOIL-BENTONITE SLURRY CUTOFF WALLS

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ABSTRACT

Model soil-bentonite cutoff walls roughly 508 mm (20 inches) in diameter, 559 mm (22 inches) in height and 102 mm (4 inches) thick were constructed and tested in an instrumented tank. The effects of overburden pressure (vertical consolidation) and hydraulic gradient (horizontal consolidation) were investigated followed by tests to evaluate the potential for closure of artificial windows representing small pockets of entrapped bentonite slurry in the backfill.

The average hydraulic conductivity of one model was measured for three hydraulic gradients under each of three applied overburden pressures. Decreases in conductivity were observed for incremental increases in both overburden pressure and hydraulic gradient as well as their combined effect. The tests were interrupted on two occasions by hydrofracture near the base of the model. A reduction in effective stress with increased depth in the model wall was evidenced by unit weight, water content and vane shear strength data. By incrementally increasing overburden pressure it was possible to "heal" two slot-like windows in a subsequent wall suggesting that in situ consolidation of the backfill may serve to eliminate minor as-built or chemically-induced hydraulic defects in real slurry walls.

INTRODUCTION

Slurry trench cutoff walls were first used in the United States in the early 1940's. Since that time, their use has become more widespread and now includes application as hydraulic barriers to control the movement of contaminated groundwater from hazardous waste disposal sites. Each application is unique and requires site-specific engineering evaluation. Nevertheless, the current state-of-the-art involves fundamental concepts, performance criteria, and methods common to all applications.

One area of special interest deals with questions of in situ consolidation of soil-bentonite backfill after placement. If significant consolidation does occur after construction, the average hydraulic conductivity of the barrier may be significantly different from that measured in the laboratory during the design and construction phases. Moreover, the finished barrier may have an inherent ability to eliminate minor construction defects (via consolidation) given sufficient time. Field observations suggest that only limited in situ consolidation may occur (evidenced by lack of subsidence of the backfill surface) which, in turn, suggests that friction between the backfill and the soils comprising the walls of the cutoff trench may strongly affect the vertical distribution of effective stress in the backfill.

An experimental tank in which model soil-bentonite walls could be constructed and tested under various hydraulic and surcharge loading conditions was constructed for this study. The tank accomodates circular cutoff walls roughly 559 mm (22 inches) in height, 102 to 152 mm (4 to 6 inches) thick, and up to 610 mm (24 inches) in diameter. The tank is of stainless steel construction and employs a pneumatic bladder system to vertically confine and consolidate the model wall during permeation in the horizontal direction. A schematic of the system is shown as Figure 1. Although relatively small and constructed using non-typical methods (described later), the models were representative of real soil-bentonite slurry walls in most other respects.

CONSTRUCTION AND TEST METHODS

A total of three model walls were constructed and tested during the course of this study. The first model was used for preliminary "shakedown" testing of the system. The second model was built to study the effects of surcharge pressure and hydraulic gradient on hydraulic conductivity. Testing involved the sequential application of three hydraulic gradients (i = 21, 42, 83) under effective overburden pressures of 41.4, 82.7 and 165.5 kPa (6, 12, 24 psi) as measured at the surface of the wall. The third wall was used to investigate the surcharge pressure necessary to close two slot-like windows during permeation. The remainder of this article describes the latter two models and the methods and results.

Both models comprised a soil-bentonite backfill designed for a target hydraulic conductivity of 1.0 x 10^{-7} cm/sec under nominal levels of consolidation and low hydraulic gradients. The backfill consisted of 1% ordinary (unaltered) bentonite in a base soil of approximately two-thirds fine to medium brick sand and one-third clay of moderate plasticity (CL classification per USCS) which contained minor amounts of silt and fine sand.

The model walls were constructed between two concentric PVC (polyvinyl chloride) slip forms representing the walls of a circular cutoff trench. The forms were positioned in the tank and backfilled with clean fine sand in 102 mm (4 inch) lifts creating an empty 102 mm (4 inch) wide annular space between the forms. This space was then filled with a 5% bentonite: water slurry (weight:volume basis) comprising the same bentonite used in the soil-bentonite mix. The soil-bentonite backfilling operation varied slightly for differ-

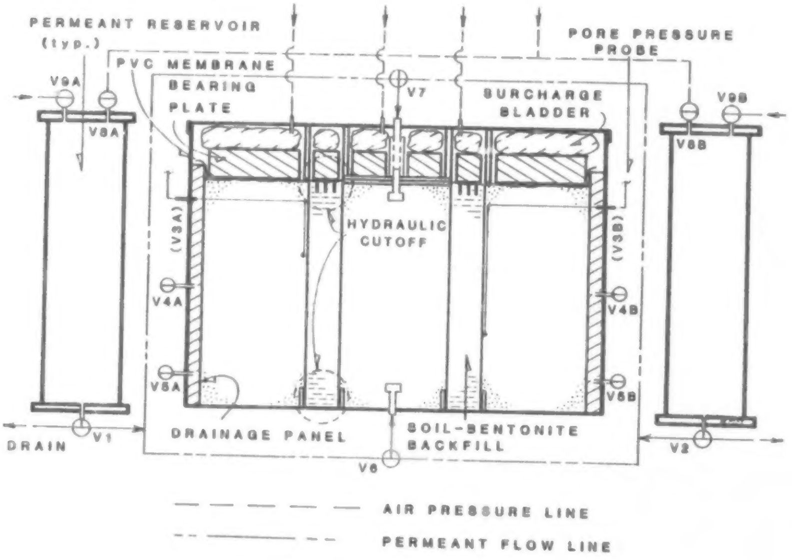


Figure 1. Schematic of the slurry wall tank system.

ent models but generally involved raising both forms about 102 mm (4 inches), allowing the bentonite:water slurry to penetrate the sand and form a surface filtration slurry seal, and then backfilling with soil-bentonite using a pressurized tremie pipe. This general procedure was repeated until the surface of the model wall was level with the surface of the center core of sand (sand encircled by the model wall) and outer ring of sand (sand encircling the model wall).

After construction, the model was readied for testing by installing a combination membrane/hydraulic cutoff over its surface and positioning concentric load-bearing plates over each element of the model (core sand, soil-bentonite wall, outer ring of sand). This arrangement allowed for differential loading and consolidation of the soil-bentonite wall relative to the adjacent sand bodies. The surface membrane/hydraulic cutoff over the top of the soil-bentonite wall was designed to promote horizontal flow through the wall during permeation and eliminate leakage over the top of the model. The cutoff system comprised three concentric PVC rings bonded to the PVC membrane and forced into the surface of the soft soil-bentonite. A similar configuration involving two cutoff rings was used on the bottom of the model as well. Schematics of both the top and bottom cutoffs appear in Figure 2.

The typical testing procedure used in evaluating the effects of overburden pressure and gradient involved saturation of the sand elements of the model, application of a selected surcharge pressure, consolidation of the soil-bentonite wall under the applied surcharge (time estimated from conventional consolidation tests performed on the backfill material), application of the design hydraulic head pressure at both the top and bottom of the saturated center core of sand (Figure 2), and the measurement of hydraulic head and volumetric inflow at prescribed time intervals.

This test procedure was performed for the three hydraulic gradients under each of the three overburden pressures reported earlier. In each case, equilibrium flow conditions were established before applying a new set of test conditions.

Similar procedures were used in the construction and testing of the third model wall to evaluate the closure of artificial slot-like windows via surcharge pressure. The slots were intended to model macro-defects such as small pockets of entrapped slurry remaining after construction of the wall. Two slots approximately 7.9 mm (5/16 inch) wide by 1.6 mm (1/16 inch) high were cut into the third wall after preconsolidation under an effective overburden pressure of 41.4 kPa (6.0 psi) as measured at the surface of the wall. The windows were positioned 180° apart at a depth of about 127 mm (5 inches) below the top of the wall. Both ends of each slot were covered with a fabric-wrapped wire mesh to prevent washing the core sand into the slot during permeation. The test procedure involved incremental increase of overburden (surcharge) pressure until the slots were effectively closed as evidenced by a return to the predetermined baseline hydraulic conductivity of the model.

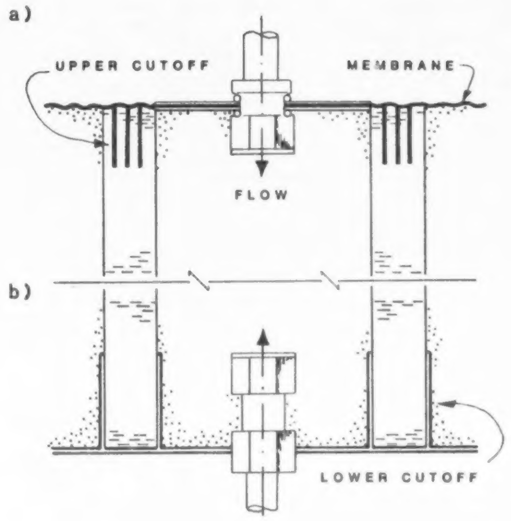


Figure 2. Schematic of a) surface membrane and upper hydraulic cutoff, b) lower hydraulic cuttoff.

The method used to compute hydraulic conductivity was the same for the overburden pressure/hydraulic gradient series of tests and the single window closing test. Using measured values of total head and the geometric constants of the models, the average hydraulic conductivity was computed using the falling head relationship:

$$k = \frac{a \cdot L}{A \cdot t} \ln \frac{h_0}{h_1}$$

where: k = hydraulic conductivity (cm/sec)
a = cross-sectional area of permeant reservoir (cm^2)
L = thickness of the wall (cm)
A = cross-sectional area of the wall perpendicular to the direction of flow (cm^2)
h_0 = initial total hydraulic head (cm)
h_1 = final total hydraulic head (cm)
t = time interval between two readings (sec)

RESULTS AND DISCUSSION

Overburden Pressure and Hydraulic Gradient

The testing of the second soil-bentonite wall, termed Sequence 2 tests, involved staged increases of overburden pressure and hydraulic gradient over a period of six months, followed by sampling and measurement of unit weight, vane shear strength and moisture content as a function of depth in the model. Figure 3 represents a composite of Sequence 2 hydraulic conductivity results for the six sets of test conditions indicated (2(a) through 2(g)). All six curves are of similar shape and for the most part their relative positions present a logical picture of decreasing equilibrium hydraulic conductivity with increasing hydraulic gradient for any given overburden pressure. Note however, that test 2(c) is missing, test 2(f) was terminated prior to achieving equilibrium conditions, and that data for tests 2(f) and 2(g) do not conform to the otherwise logical trend described above. The explanation appears in Figure 4 which presents a chronological summary of the final equilibrium conductivities measured for each set of test conditions.

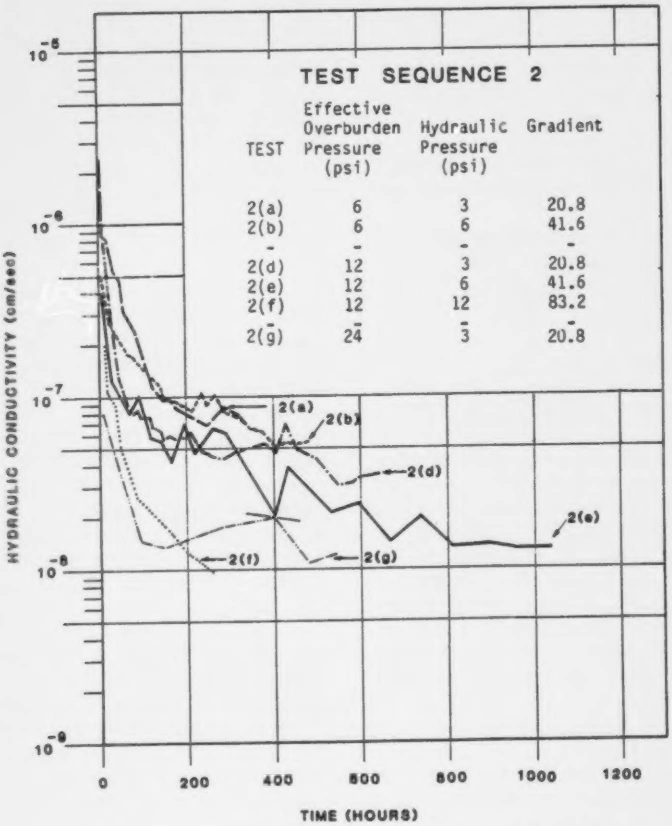
In the typical test, the wall model exhibited a high initial hydraulic conductivity represented by an open triangle, then dropped off and gradually approached the final equilibrium value designated by an open circle. Two incidences of hydrofracture, one resulting from a ruptured surcharge bladder (loss of applied overburder pressure), are indicated by solid triangles.

The first incidence of hydrofracture occurred near the end of test 2(b) strongly suggesting that the effective stress at some point in the model (presumably near its base) was less than the effective overburden pressure. Because of the hydrofracture, test 2(c) was not attempted. Instead, test 2(d) involving a doubling of applied overburden pressure and a reduction in hydraulic pressure was initiated in an attempt to heal the first hydrofracture. Test 2(f) also suffered a rupture of the surcharge bladder resulting in a second hydrofracture of the soil-bentonite wall.

To estimate the extent of damage, test 2(g') was conducted at overburden and hydraulic pressures matching those of test 2(d). As shown in Figure 4, the results of test 2(g') did not match those of test 2(d), having an equilibrium hydraulic conductivity almost an order of magnitude higher. These data clearly indicate permanent damage of the model as a result of the two cases of hydrofracture. Results for test 2(g), however, illustrate that a large increment in surcharge pressure can partially offset the effects of hydrofracture.

In the field, both vertical and horizontal consolidation of the backfill occur simultaneously. The equilibrium conductivity values reported in Figure 4 may therefore be regarded as representing the combined effect of both vertical (surcharge) and horizontal (hydraulic gradient) consolidation stresses for the test conditions applied.

Except for test 2(g), the data suggest a logical trend of decreasing equilibrium hydraulic conductivity as a function of either increasing surcharge pressure (compare results of tests 2(b) and 2(e)) or increasing hydraulic gradient compare results of test 2(a),(b) and 2(d),(e),(f)). Although the observed trend is logical, the data fail to reflect the correct magnitude of change in hydraulic conductivity between successive tests in several cases. For example, the actual equilibrium hydraulic conductivity for test 2(d) (and therefore also for all subsequent tests) is lower than reported. As described earlier, the reason is that hydrofracture permanantly changed the properties of the wall, thus artificially offsetting groups of data measured after hydrofracture from other groups of data measured before hydrofracture. In terms of internally consistent groups of data then, the following two sets of tests may be recognized: 2(a),(b) and 2(d),(e),(f) (as



TEST SEQUENCE 2

TEST	Effective Overburden Pressure (psi)	Hydraulic Pressure (psi)	Gradient
2(a)	6	3	20.8
2(b)	6	6	41.6
-	-	-	-
2(d)	12	3	20.8
2(e)	12	6	41.6
2(f)	12	12	83.2
2(g)	24	3	20.8

Figure 3. Sequence 2 hydraulic conductivity test results

projected).

The equilibrium values shown in Figure 4 represent the combined effect of vertical and horizontal consolidation. Plotted in terms of combined (total) vertical and horizontal effective stress with the corresponding permeability data on an arithmetic scale, these same data would appear as shown in Figure 5. The plot very closely resembles a typical void ratio versus pressure curve obtained from a conventional consolidation test. The interpretation of the data is also similar in that beyond a certain point, the rate of change in permeability (or void ratio) greatly diminishes for a unit change in total stress, i.e., the material becomes more difficult to consolidate the more consolidated it is. Although the two sets of data (2(a),(b) and 2(d),(e),(f)) are not strictly compatible as explained earlier, they do reflect a logical and expected trend, and permit the following general observations:

- Test set 2(d),(e),(f), exhibits greater changes in hydraulic conductivity for the same change in hydraulic pressure reflecting the reconsolidation or "healing" of a soil-bentonite wall that had been damaged (hydrofractured) to an undetermined extent.

- The change in equilibrium hydraulic conductivity due to either a unit change in hydraulic head pressure or a unit change in surcharge pressure can be on the same order of magnitude, i.e., the effect of horizontal (gradient-induced) consolidation can be as large as the effect of vertical (surcharge) consolidation for a comparable pressure change.

After the completion of Sequence 2 test 2(g) reported in Figure 4, the tank was opened to permit visual inspection of conditions and allow for sampling and testing of the consolidated backfill. The sampling included undisturbed tube samples and water content samples of the soil-bentonite at various locations and depths. Testing involved measurements of unit weight, vane shear strength, and water content. Data for these parameters appear as a function of depth in Figure 6.

Despite the semi-qualitative nature of these data (due to hydrofracturing of the model) they clearly demonstrate that the effective overburden stress applied at the surface of the wall did not act over the full depth of the wall. In other words, overburden stress was dissipated with depth, with the net result that the final values of dry density and vane shear strength are highest near the top of the wall (highest degree of consolidation) and final water content is highest at the base of the wall (lowest degree of consolidation).

Window Closure

The probability of "windows" existing in a field-scale slurry wall, whether representing an as-built condition related to materials or construction technique, or resulting from long-term exposure to chemicals, is not known. Presumably, undetected subsurface windows might develop due to entrapment of slurry or sloughed trench wall materials within the backfill during the backfilling operation. According to Evans et al,(1) the probability of such entrapments along the surface of the advancing soil-bentonite "mud wave" is high. Moreover, limited evidence of these types of "windows" was observed during the post-test inspection of the model.

After Sequence 2 testing a third wall

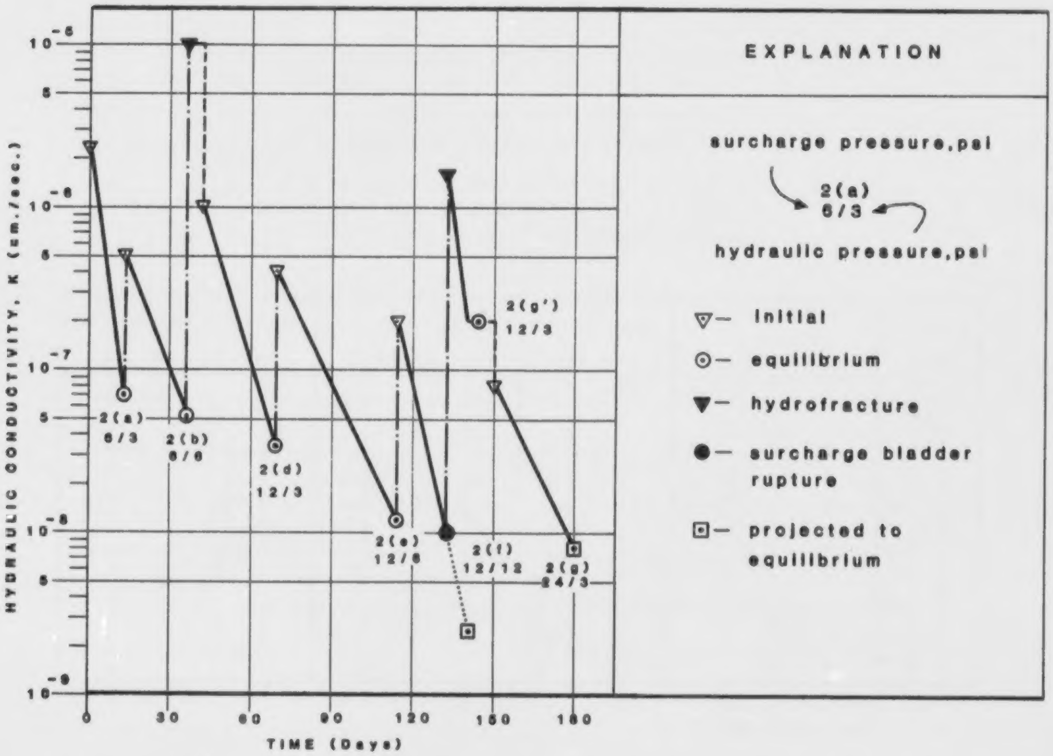


Figure 4. Chronology and results of Sequence 2 hydraulic conductivity tests.

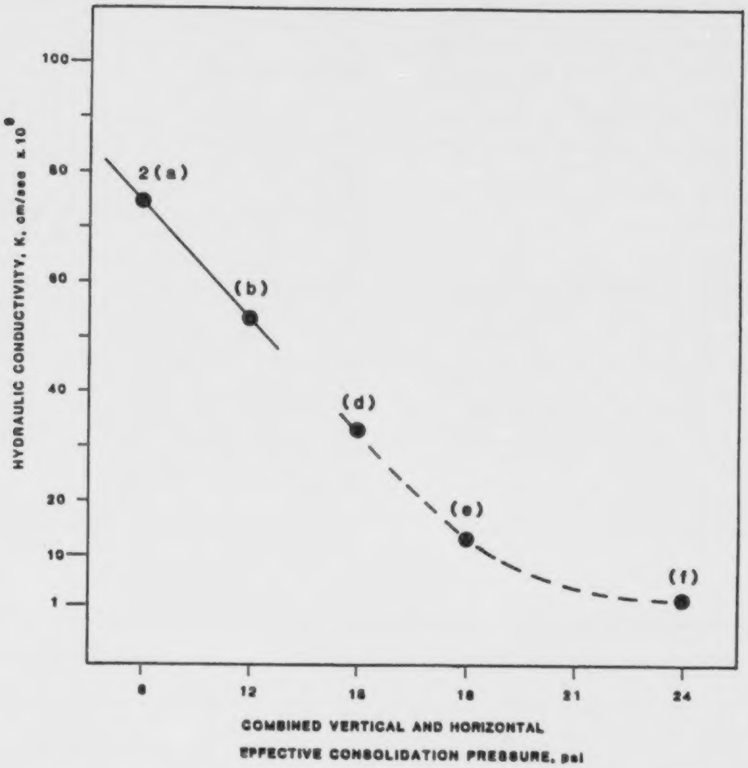
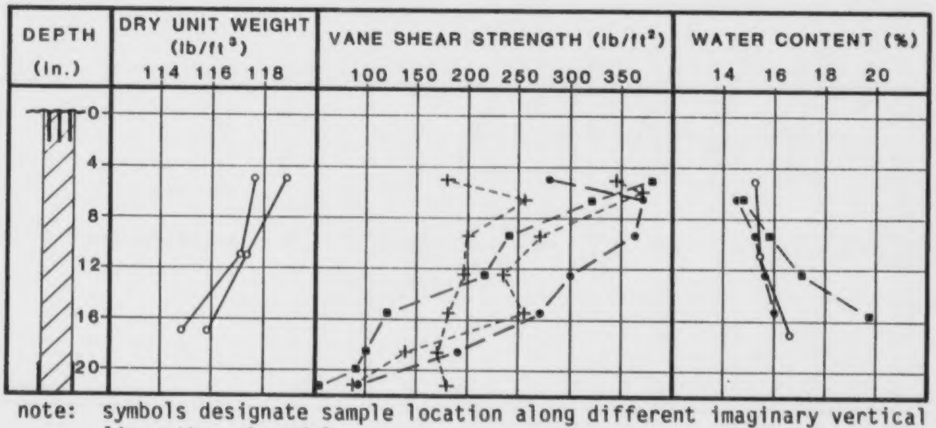


Figure 5. Equilibrium hydraulic conductivity as a function of combined effective overburden (vertical) and hydraulic (horizontal) pressure.



note: symbols designate sample location along different imaginary vertical lines through model

Figure 6. Results of tests on soil-bentonite backfill after completion of Sequence 2 testing.

was constructed for the window closing test. Before the slot windows were formed the new wall was preconsolidated under an effective overburden pressure of 41.4 kPa (6 psi) and a hydraulic pressure of 20.7 kPa (3 psi) representing a gradient of 20.8. Baseline (no window) results for test 3(a) are shown in Figure 7. The hydraulic conductivity versus time curve has the typical shape of the previous Sequence 2 data shown in Figure 3.

After establishing a baseline or reference value of hydraulic conductivity, the two slot windows were formed at the locations and depths previously described. Overburden pressure was then gradually increased causing the apparent hydraulic conductivity of the model to decrease until the windows had been effectively closed as evidenced by a return to the measured baseline conductivity. These data also appear in Figure 7 and show that the average conductivity of the model was lowered relative to the target baseline value under the final set of test conditions. For this reason it was not possible to identify a specific threshold value of surcharge pressure necessary to heal the two slot windows.

The success of this window closing test has important ramifications for real

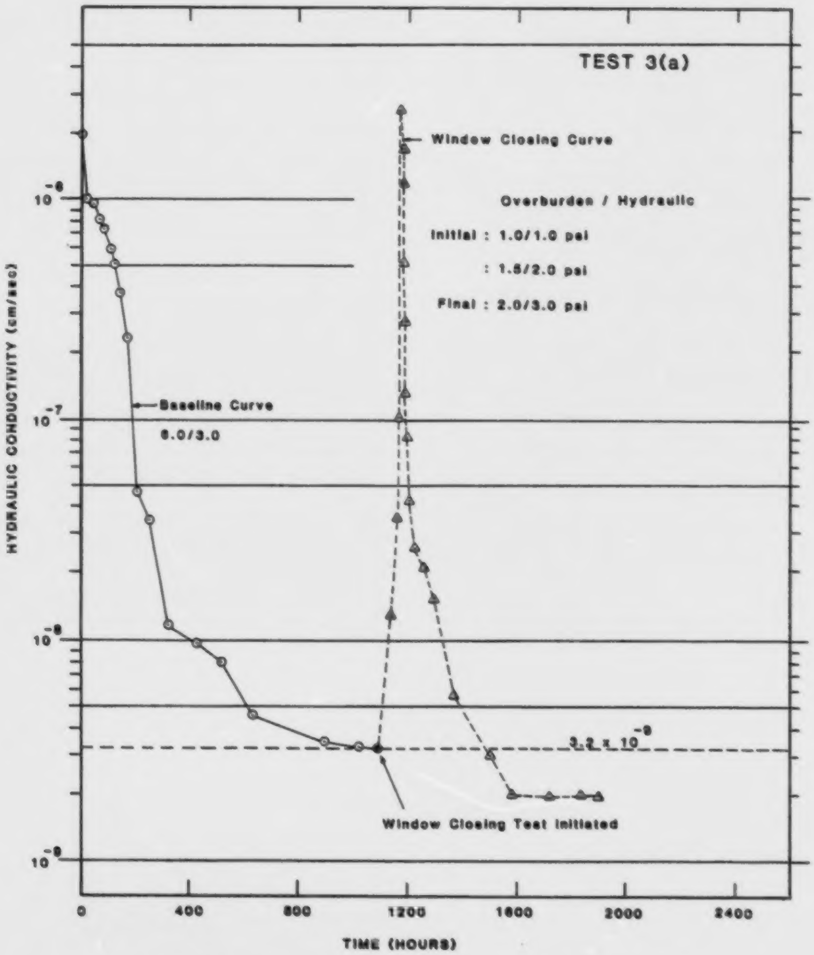


Figure 7. Baseline and window closing hydraulic conductivity test results.

slurry walls. It means that the effective overburden pressure in the wall may serve to close residual slurry windows and may even close a multitude of micro shrinkage cracks that may develop in the backfill over the life of the barrier due to the effects of chemical leachates.

ACKNOWLEDGEMENTS

The research described herein was supported wholly by the Land Pollution Control Division of the U.S. EPA Hazardous Waste Engineering Research Laboratory under contract #68-03-3210 to the Department of Civil and Environmental Engineering, University of Cincinnati. Appreciation is expressed to project officer Joseph K. Burkart and Work Assignment Manager Naomi P. Barkley for their administrative and technical support. The authors also wish to acknowledge and thank graduate student Jong Jen (Steve) Lin for his enthusiastic dedication to the work and Frank E. Weisgerber for his technical contributions. Finally, we gratefully acknowledge base operations manager Gerard Roberto for his considerable efforts on behalf of this project and others at the Center Hill Solid and Hazardous Waste Research Facility.

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EXPERT SYSTEMS TO ASSIST IN DECISIONS CONCERNING LAND DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

In FY'84 the Hazardous Waste Engineering Research Laboratory successfully developed a small proof-of-concept expert system to assist in interpretation of chemical immersion test (EPA Method 9090) data for PVC liner materials. This was the beginning of an orderly progression of efforts to assess the feasibility of using expert systems to assist in permit reviews for hazardous waste land disposal sites. Permit review decision areas amenable to expert system applications have been identified and several systems are in various stages of development and testing. The rationale for this approach to provide decision support aids for permit review include the complexity of the required engineering evaluations; availability of extensive relevant research results and known subject-specific specialists (experts); concern that permit reviewers do not have all of the required expertise and that they have little, if any access to subject specific specialists; concern that the reviewers do not have sufficient time to assimilate all regulatory policy and research information; and concern that decisions may not be consistent among reviewers or with EPA regulations and policies. The decision areas selected for expert system development and the progress on the ongoing development efforts will be presented.

INTRODUCTION

Review of permits for land disposal of hazardous wastes requires numerous decisions concerning technical and policy issues. Some require interpretation and application of information in research reports, others involve interpretation and evaluation of specialized test data, and others involve assessment of compliance with latest regulatory policies. Specialized knowledge concerning a number of technical areas and a broad base of environmental regulatory experience are necessary to adequately perform these reviews. This need for current knowledge and background in addition to the concern that reviews be consistent (i.e., permits are judged the same by all reviewers) prompted our interest in expert systems.

Expert systems are computer programs (software) designed to provide advice concerning specialized areas. The design objective of the programs is to emulate the advice of subject specialists by incorporating the decision rules or criteria that they use in terms of IF --- THEN statements. For example, IF the carbon black content of an HDPE liner is less than 2 percent THEN the liner is inappropriate. Two characteristics of these programs differentiate them from traditional programs, namely (1) they are essentially large pattern matching routines that seek a solution (advice) that corresponds to the pattern of input data and (2) the program logic is separated from the rules (IF --- THEN statements) to facilitate ease of rule modification or refinement. Like traditional programs these systems can perform engineering and statistical calculations, but these are not the primary feature of these systems.

This paper presents the history, current status, and future direction of the expert systems development program supported by the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory. The development methods being used and some of our experiences are also presented.

HISTORY OF EXPERT SYSTEMS DEVELOPMENTS

In 1984 a small proof-of-concept expert system was developed to assist in assessment of chemical compatibility of PVC liner materials based on chemical immersion test (EPA Method 9090) data. This system demonstrated that at least for this specific application it is feasible to extract sufficient information from an expert to formulate advisory rules for some decisions that must be made by permit reviewers. This system contained 20 rules and was written in BASIC for the IBM PC microcomputer. To determine what other permit review decision areas would be amenable to expert system applications, a Requirements Study was initiated. Other issues addressed were development strategy, software and hardware requirements, and associated resource requirements. Table 1 presents the prioritized list of decision areas identified by this project, which was completed in the fall of 1985. In order to facilitate compatibility among the systems designed to provide assistance in the different decision areas, and to facilitate information sharing among them, it was recommended that a supervisory system with decision-specific submodules be developed to address permit review. It was also recommended that development be performed on AI dedicated hardware with specialized software due to the limitations of the PC-based expert systems software at the time. The former recommendation was rejected due to the concern that the deadlines for performing most permit reviews would be past before a comprehensive permit review system could be built, hence the strategy of developing independent modules to address individual, narrowly defined decision areas. The latter recommendation was rejected due to the concern over potential high equipment costs (for development and possibly for running the systems) and the uncertainty that it would be feasible to develop software on the specialized hardware for use on the available micro-computers. Our objective was to make the systems available for use by everyone in the EPA or the states responsible for permit review. Due to these concerns and the rapidly advancing capabilities of micro-computer based expert systems languages and shells the decision was made to develop the systems on the PC for use on the EPA standard IBM PC/AT microcomputers. Also the goal of wide distribution of the systems has been an important factor in selection of particular microcomputer software. Strong preference for minimal licensing costs for run time versions in addition to flexibility for tailoring to particular applications, have been the driving considerations for software selection. The recommendations of the Requirements Study concerning decision areas provided direction for initial development efforts and raised the issues of development strategy and software/hardware selection for consideration and resolution.

The initial proof-of-concept PVC liner resistance system was redone by an EPA contractor. It was expanded to include advisory rules for HDPE and CSPE liner materials and refined by incorporating the advice of additional experts. This system is ready for limited use by permit reviewers. A Waste Analysis advisory system has also been developed and is ready for limited use. Current development efforts include systems to assist in evaluation of Closure Plans, Surface Impoundments, and Site Selection and to assist in screening of control technologies for CERCLA sites. Each of these systems is described in further detail later in this paper.

SYSTEM DESCRIPTIONS

The FLEXIBLE MEMBRANE LINER RESISTANCE system includes rules to assist in interpretation and evaluation of chemical immersion (EPA Method 9090) data for PVC, HDPE, and CSPE liner materials. The primary input data for the system are physical property measurements obtained during a four-month time period; the 9090 test requires immersion of coupons of the liner material in the waste to be disposed. Information is also included concerning the carbon black content (for HDPE materials), intended service life, etc. Based on this input the system determines if there is evidence that the proposed liner material may not be resistant to the wastes that will be deposited at the site. An example of input data is presented in Table 2 and the resulting conclusions are shown in Table 3. The data are entered on Lotus 1-2-3 type screens and can be edited, saved, plotted, and/printed out on the screen or hard copy. This is different from the typical interactive, or question-driven, input of many expert systems. Advice corresponding to any set of input data is derived by transferring the data and some simple statistics (means, percent changes, etc.) to an expert system written in Arity Prolog. Conclusions that a liner material is not chemically resistant to the subject waste/leachate are presented separately for each physical property examined. Nothing is stated concerning those properties that do not indicate a failure to be resistant. For example, in the sample data in Table 2, since weight does not change over time, nothing is said concerning weight change in the conlusions in Table 3. Excessive scatter in the data, which makes trend analysis uncertain, is also noted as illustrated by tensile strength. All of the systems have been developed for application on an IBM PC/AT microcomputer. This system is currently being reviewed by the Office of Solid Wastes in preparation for release and introduction to the EPA Regional Offices and the States in performing permit reviews of land disposal facilities.

This system was developed by an EPA contractor and is an expansion and refinement of the original prototype system developed by the Laboratory. Since the expert used as the resource for the initial system is a well known recognized expert in the field of flexible membrane testing, he was also used as one of the subject specialists (experts) and consultant for this phase of the development effort. The fact that he gave different responses to questions by the contractor personnel than to the same questions by the EPA person, and did not recall the advice recorded by the EPA person, illustrates the importance and difficulty of acquiring expert opinions. This problem has been alleviated in this follow-up system by acquiring the input of multiple experts and by comparisons of their advice with that of the finalized system on sample test data. Further testing of the rule bases and software is also being performed by the Office of Solid Waste to insure compliance with regulatory policies and guidance documents, to identify any errors in the software, and insure that the users' manual is correct and adequate. Thorough documentation, including identification of the source for each rule in the rule base, is a requirement for all of the systems.

The WASTE ANALYSIS PLAN EVALUATION SYSTEM assists in the identification of chemical incompatibilities that may occur when different waste chemicals are handled, stored, treated, or buried together. It also recommends the appropriate sampling equipment and analytical methods for monitoring the waste stream. The knowledge base (rules and information) for this system was developed by the expert who prepared the manual entitled "Waste Analysis Plans: A Guidance Manual" for the Office of Solid Waste. Other resource materials included regulations in 10 CFR Part 21 "Identification and Listing of Hazardous Wastes" and 40 CFR 264 Waste Management Facility Regulations; and guidance from regulatory personnel in the Office of Solid Waste and permit reviewers from two EPA Regional Offices. This system was also developed in Arity Prolog for application on the IBM PC AT microcomputer. It has been tested in two of the EPA Regional Offices and one state.

The waste analysis evaluation system will be finalized by the EPA contractor by early spring of 1987 and submitted to the Office of Solid Waste for Review and testing. This system is effectively an intelligent data base system that facilitates implementation of the evaluation procedures specified in the Waste Analysis Plan Evaluation Document prepared by OSW. As such it helps to illustrate one of the uses of expert systems methods. One of the primary features of the system is the identification of chemical incompatibilities among the waste compounds. Typically this would be done by a professional chemist and/or by consulting available tables. Many of the permit reviewers are not chemists, however, and looking up every pair of chemicals in an appropriate table is time-consuming. The waste analysis system reduces the time for this determination, which is another reasonable purpose of expert systems.

The SUBSIDENCE EVALUATION SYSTEM was developed to identify waste characteristics, disposal procedures, climatic conditions, etc. that increase the risk of differential subsidence of a landfill after closure. This system incorporates the observations and insights of coprincipal investigators on an EPA-supported project to identify and evaluate the causes of post-closure differential subsidence. As are the earlier described systems, this one is also written in Arity Prolog for application on the IBM PC/AT microcomputers. The rules for this system are ready for inclusion as part of a system to evaluate the adequacy of proposed cover systems.

The subsidence system was a learning experience by the EPA staff to assess the feasiblity of summarizing the results of a recently completed research project in terms of an expert system. As a result of this effort, one can learn to understand the factors that contribute to post-closure differential subsidence by either reading the final project report or using the parallel expert system. This further illustrates potential applications for expert systems techniques. A diskette could be provided with each major research report or as a stand-alone product. The expert system would facilitate use of the basic material and the final report would provide further discussion and/or resource materials.

The CONTROL TECHNOLOGY SCREENING SYSTEM was designed to assist in screening of technologies to contain or remove hazardous wastes from CERCLA (Superfund) sites. The technologies included in the system database are arranged in a four-level hierarchy. These levels consist of 1) generic action (containment or removal), 2) action class (e.g., capping, subsurface barriers, etc.), 3) technology class (e.g., single layer caps, horizontal barriers, vertical barriers, etc.), and 4) distinct technologies (e.g., soil liner cap, synthetic liner cap, slurry wall, etc.). The rules for this system were developed from information contained in available reports and documents published and/or supported by the EPA (see Table 3). The system is not complete and ready to use since it contains a number of information gaps and needs refinement. It is an excellent prototype system that demonstrates the potential for this type of application. It has also been written in Arity Prolog for application on the PC AT microcomputer.

The technology screening system is being directed towards the need of the EPA Site Coordinators responsible for initial feasibility investigations of Superfund sites. In addition to its basic screening role, it has features that could be used as a training tool and information resource. Thorough Help screens are included to define and explain terms and selection criteria, and the rules for assessing suitability of a particular technology are presented in self-explanatory terms. The input data for each run can be saved and selectively modified as part of a sensitivity analysis. This system, which is based on the information abstracted from mutiple resource materials, illustrates the feasibility of using expert systems concepts to integrate information from multiple sources into a unified information resource.

The SURFACE IMPOUNDMENT SAFETY ANALYSIS SYSTEM is being designed to provide user-friendly access to available analytical routines for estimating safety of selected components of surface impoundments. The system will also assist in interpretation of the safety factors that results from the calculations. The development language or expert system shell has not yet been decided but it will likely be written in Insight 2 (a PC expert system shell) with the analytical routines written as Fortran subroutines that are accessed thru links written in C. The delivery system will be written for application on the IBM PC AT microcomputer. Scheduled completion is late summer or fall of 1987.

The CLOSURE PLAN EVALUATION SYSTEM is being developed to assist in review of closure plans (for land disposal sites that will close due to failure to apply for a part B permit or failure to receive approval of their part B permit) and permits for closure (for land disposal sites that submit a part B and receive approval). The initial system will not be applicable to "clean" closures for surface impoundments. The system has been divided into the following 6 components:

1. Cover systems
2. Runon/runoff control
3. Final vegetative cover
4. Ground-water monitoring program
5. Leachate collection and treatment systems
6. Scheduled maintenance and monitoring of all systems

Development is being phased and staggered. Initial efforts will be devoted to initiation and development of one system. Midway through the time for completion of the first project, the second one will be initiated. When the first system is finalized the third one will be initiated while efforts on the second continue. It is anticipated that the first system will be completed by the first of August of 1987 with each successive system due for completion 2 months after completion of the former, i.e., the second is scheduled for completion by the first of October, 1987, the third by the first of December, 1987, etc. The total time for the 6 modules is scheduled at 14 months. The delivery machine will be the IBM PC/AT microcomputer with minimal required enhancements such as a graphics card. The decision concerning software has not yet been made.

DISCUSSION

All of the expert systems supported by the Hazardous Waste Engineering Research Laboratory address issues related to containment of hazardous wastes in a land disposal site or removal to another site. The decisions addressed by each are sufficiently limited in scope that the systems are small enough for implementation on the standard IBM PC/AT microcomputer. The primary focus of the systems are technical issues that have been researched by the Laboratory during the past years. Hence EPA-sponsored research reports have been a major source of information for knowledge-base formation for a number of the systems. That is one reason we believe that expert systems (or knowledge-based systems) can play a significant role in terms of automated technology transfer systems for the Laboratory.

Based on our experience, prototype systems can be developed to address relevant questions without a major commitment of resources and time. Some of the smaller inhouse systems were developed within 2 or 3 months by one person assisted by a microcomputer specialist. Development of prototype systems, however, is not the major task. The major effort is to prepare a finalized system for general use by decision officials both within and outside the Agency. Some of the time-consuming and difficult tasks include knowledge-base refinement to address latest research results, policy considerations, and user needs and desires; testing the knowledge bases to insure they reflect the opinions of the experts or advice contained in the source materials; testing of the source code to insure freedom from coding and programming errors; documentation of the source code and preparation of an users' manual; maintenance and refinement of the systems; and provision of readily available and accessible user support. In order to insure that the systems satisfy the needs of the user community, we are working interactively with the users as the systems are initially conceived, developed, and refined. One of the systems (Flexible Membrane Liner Resistance) is being tested by comparing the conclusions of the system on sample test data with those reached by the experts without assistance from the system. All rules are being documented by source (expert or specific report citation). The other issues are being discussed with representative from the Office of Solid Waste but have not yet been resolved.

Based on the success of our development efforts, responses from the user community, and the interests expressed by management and regulatory personnel, the next major expansion area will be treatment technologies. This will include screening of treatment methods or technologies for the RI/FS process for Superfund sites and/or remediation of RCRA sites, evaluation of treatment test data (for example trial burn data), and evaluation of proposals for particular treatment regimens to handle particular waste streams.

CONCLUSIONS

It is feasible to develop usable and useful expert systems. Expert systems appear to offer significant opportunities for insuring expedient implementation of latest technologies, compliance with regulatory policies, and decision consistencies. Hence we expect to continue efforts to complete systems under development, maintain ongoing systems and develop new ones to assist in other amenable decision areas.

TABLE 1

PRIORITIZED LIST OF PERMIT REVIEW DECISION AREAS AMENABLE TO EXPERT SYSTEM APPLICATIONS (As Of December 1985)

Priority 1

- Facility Closure Plans
- Facility Location Information
- Synthetic Liner Design
- Dike Design and Construction

Priority 2

- Lower Soil Liner Design
- Secondary Leachate Collection
- Primary Leachate Collection
- Facility Post-Closure Plan
- Landfill Run-on Control System Design
- Lower Soil Liner Construction
- Landfill Run-off Control System Design
- Waste Analysis Plan

Priority 3

- Plan for Management of Units Associated with Landfill Run-on and Run-off Control Plan
- Chemical and Physical Analysis of Hazardous Waste to Be Handled
- Prevention of Overtopping
- Landfill Wind Dispersal Flow Control Plan
- Construction Quality Assurance Plan
- Synthetic Liner Construction (upper and lower)

Priority 4

- Inspection Plans
- Plans for Preparedness and Prevention
- Contingency Plans
- Precautions Taken to Prevent Ignition or Reaction of Wastes
- Planned Traffic Pattern
- Closure Cost Estimates and Financial Assurances
- Post Closure Cost Estimates and Financial Assurances

Priority 5

- Lists of Wastes to be Placed in each Surface Impoundment/Landfill
- Certification by Qualified Engineer of Dike's Integrity
- General Facility Description
- Procedures and Equipment to Prevent or Mitigate Hazards
- Training Program
- Facility Deed Documentation
- Insurance Policies
- Coverage by State Financial Mechanisms
- Topographic Map for the Facility and Environment

TABLE 2

SAMPLE DATA FROM 9090 TESTING OF HDPE LINER MATERIALS IMMERSED IN A HYPOTHETICAL WASTE

WEIGHT (grams)

	Time (months)		Time (months)		Time (months)		Time (months)	
Sample Coupon	0	1	0	2	0	3	0	4
1	1.83	1.83	1.87	1.87	1.85	1.86	1.84	1.85
2	1.87	1.87	1.87	1.87	1.85	1.86	1.83	1.84
3	1.85	1.86	1.87	1.88	1.86	1.87	1.87	1.87
4	1.85	1.86	1.84	1.84	1.87	1.87	1.87	1.87
5	1.87	1.88	1.87	1.88	1.87	1.87	1.86	1.87
Average	1.86	1.86	1.86	1.87	1.86	1.86	1.85	1.86
% Change		0.19		0.28		0.41		0.25

TENSILE AT BREAK (lb/in)

	Time (months)				
Sample Coupon	0	1	2	3	4
1	3800	2750	2450	2470	3740
2	3800	3650	2520	2640	3720
3	3800	4490	3810	2570	2470
4	3800	4190	2570	2670	4560
5	3800	4020	3490	2870	3550
Average	3800	3820	2958	2644	3610
% Change	0.00	0.53	-22.16	-30.42	-5.00

MODULUS (lb/in)

	Time (months)				
Sample Coupon	0	1	2	3	4
1	82900	96000	87500	71500	60400
2	84100	95500	86200	72000	64200
3	83000	93000	87500	79500	61300
4	84900	93800	89000	74200	62300
5	85200	94500	85500	76500	61800
Average	84020	94560	87140	74740	62000
% Change	0.00	12.54	3.71	-11.04	-26.21

TABLE 3

CONCLUSIONS OF FLEXIBLE MEMBRANE LINER EXPERT SYSTEM FOR SAMPLE DATA PRESENTED IN TABLE 2

The liner is fundamentally inappropriate for the application.

The liner is fundamentally inappropriate for the proposed application because either initially or at some point in the immersion test one or more of the liner's key physical properties was below the minimum standards established by the National Sanitation Foundation (NSF). NSF Standard Number 54 was developed in consultation with several liner industry experts. Standard Number 54 specifies minimum values for several physical properties for HDPE liners of two thicknesses 0.08 and 0.1 inches (i.e., 80 and 100 mils). There is no NSF standard for HDPE liners of less than 80 mils.

The NSF standard requires modulus of elasticity be more than 80,000 lbs/sq in. For this applicant the modulus of elasticity is 62,000.

The immersion test results indicate that the liner is not chemically resistant to the waste/leachate.

The immersion test results indicate that the liner material is excessively softened by the waste/leachate. Excessive softening is a sign of poor chemical resistance. A liner material that softens excessively may not be able to withstand the stresses of the waste site and may fail due to tearing or puncture.

Excessive softening of the liner material is evidenced by an excessive loss in its modulus of elasticity. At a lower modulus a given force will produce a greater elongation of the material. Excessive losses in modulus suggest the potential for easier tear, puncture, and break of the liner.

The loss in molulus of elasticity was -25.21%. This is beyond the threshold limit of 25% used by many liner material specialists.

No conclusion can be made as to the chemical resistance of the liner material to the waste/leachate.

The results are inconclusive because there is excessive scatter (i.e., lack of precision) in the immersion test results.

The average standard deviation of the data for the four-month immersion is greater than 10% for the measurements of changes in:

The tensile strength at break of the liner material.

MODELING SOIL WATER MOVEMENT IN MINIMUM TECHNOLOGY WASTE MANAGEMENT FACILITIES

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ABSTRACT

The hydrology of landfills, surface impoundments, and waste piles is dominated by unsaturated flow of soil water. Unsaturated conditions normally persist in the cover, solid waste, liner system, leachate collection and removal system, and in the soil below these systems. A finite element model, UNSAT2D, developed as a generalized computer program based on the two-dimensional equation of saturated/unsaturated flow, is described. This model can be used to simulate moisture movement through a two-dimensional vertical section of a facility.

Results from a series of simulations of alternative "minimum technology" designs are discussed, with emphasis on bottom liner design and leak detection. These data show that leak rates into leachate collection and removal (LCR) systems in excess of 100 gallons/acre-day are necessary for LCR system drains to flow when constructed over three-foot thick compacted soil bottom liners with a hydraulic conductivity of 10^{-7} cm/s. LCR systems built in conjunction with composite (flexible membrane over low-permeability soil) bottom liners are significantly more effective. Time to drain flow is reduced, minimum leak rate resulting in LCR system drain flow is reduced, and leachate collection efficiency increases.

INTRODUCTION

The Hazardous and Solid Waste Amendments of 1984 require that certain landfills and surface impoundments have two or more liners designed to contain hazardous constituents, and a leachate collection system designed to promptly detect any leaks, should they occur. Similar rules apply to waste piles.

These requirements constitute the "minimum technology" for waste management facilities constructed to treat, store, or dispose of hazardous waste. To predict the effectiveness of different leachate collection and liner system designs, it is necessary to have a prior understanding of saturated and unsaturated moisture movement within such systems. A useful approach to gaining insight into the hydraulic behavior of these systems is to apply computer simulation techniques. In this way a broad spectrum of design, siting, operational, and failure scenarios may be modeled and the results used to evaluate significant factors that influence leachate collection and liner system performance.

This paper describes the computer program UNSAT2D that was developed to model saturated and unsaturated flow in landfills, surface impoundments, and waste piles. Following the description, results from a number of computer simulations are discussed in terms of leachate collection and liner system performance.

MODEL DESCRIPTION

Soil moisture movement within a facility is described by the two-dimensional equation of saturated/unsaturated soil moisture flow within a specified flow domain. A generalized representation of the flow domain Ω is shown in Figure 1. That domain is defined by the union of boundary surfaces S_1 and S_2. On the boundary surface S_1, head is specified. On the boundary surface S_2, flux is specified. The specified head and specified flux are each functions of location and time.

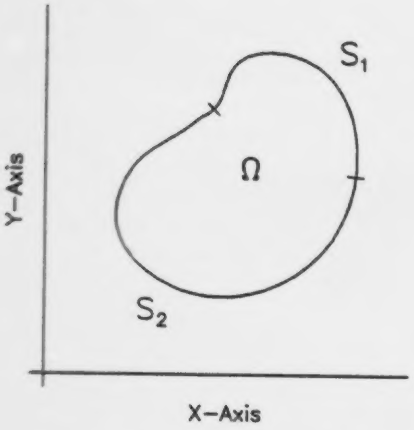

Figure 1. Diagram representative of the flow domain.

The initial and boundary value problem associated with this two-dimensional flow domain is described by the following set of equations, written in repeating index notation:

$$\frac{\partial}{\partial x_i}\left[K_{ij}(p)\frac{\partial h}{\partial x_j}\right] + N - \left[\frac{d\theta}{dp} + S_s\right]\frac{\partial h}{\partial t} = 0 \quad (1)$$

for $i = x,y$

$$h(x_i,t) = h_B(x_i,t) \quad \text{on } S_1 \quad (2)$$

and

$$K_{ij}(p)\frac{\partial h}{\partial x_i}n_i = -q_B(x_i,t) \quad \text{on } S_2 \quad (3)$$

Where h is hydraulic head, h_B is hydraulic head on the specified head boundary, K_{ij} is the hydraulic conductivity tensor, n_i is the outward normal vector on the specified flux boundary, S_s is specific storage, q_B is the flux across the specified flux boundary into the flow domain, N is a source or sink, x_i are coordinates x and y, t is time, θ is soil moisture content, p is soil moisture potential, and dθ/dp is the soil moisture capacity. Additionally, total head and soil moisture potential are related by the expression:

$$p(x,y,t) = h(x,y,t) - y \quad (4)$$

Equation 1 describes the conservation of mass at a point. To solve the partial differential equation, additional specification of the problem is needed. In particular, the solution depends on the solution domain, soil characteristics, boundary conditions, and initial conditions. The solution domain consists of the flow and time domains. The flow domain is the region Ω to be modeled that is surrounded by the boundary S. The time domain is the period over which a solution is to be obtained. Soil characteristics are the hydraulic properties of the soils, waste, and membranes. Boundary conditions are a mathematical statement of soil moisture conditions at the boundary of the flow domain. Initial conditions are the specification of pressures at the start of the time domain.

Equation 1 is nonlinear because the hydraulic conductivity (K) and soil moisture content (θ) depend on the soil moisture potential (p). For a particular soil, the K-θ-p relationship defines a pair of characteristic curves. Figure 2 shows two such pairs of characteristic curves. If the effects of hysteresis are neglected, hydraulic conductivity is a monotonic function of soil moisture potential. For all non-negative soil moisture potentials, hydraulic conductivity is

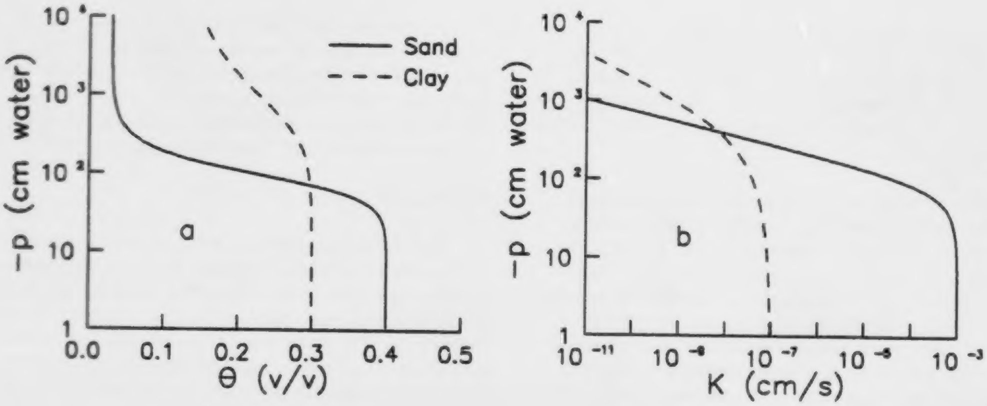

Figure 2. Volumetric moisture content (a) and hydraulic conductivity (b) versus soil moisture potential for soils used in the simulations. For sand, $\alpha = 0.3658$ ft^{-1} and $n = 3.00$. For clay, $\alpha = 0.0616$ ft^{-1} and $n = 1.59$ (Equations 5 and 6).

the saturated hydraulic conductivity. For negative potentials (positive soil moisture tensions), however, the hydraulic conductivity decreases with decreasing soil moisture potential. Likewise, the soil moisture content has a similar functional relationship to soil moisture potential. The soil moisture capacity, however, has a different functional relationship. Soil moisture capacity is zero near saturation, it is zero for large soil moisture tensions, and it has positive values between those points.

The van Genuchten equations (2) were selected to describe parametrically the unsaturated hydraulic properties of soils. These equations are:

$$\theta(p) = \theta_r + \frac{(\theta_s - \theta_r)}{[1 + (\alpha|p|)^n]^m} \tag{5}$$

$$K(p) = K_s H^{1/2}[1-(1-H^{1/m})^m]^2 \tag{6}$$

$$\frac{d\theta}{dp} = (\theta_s - \theta_r)\ \alpha^n mn(1 + |\alpha p|^n)^{-m-1}|p|^{n-1} \tag{7}$$

$$m = 1 - \frac{1}{n} \tag{8}$$

and

$$H = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{9}$$

where θ_s is the saturated soil moisture content, θ_r is the residual soil moisture content, K_s is the saturated hydraulic conductivity, α and n are parameters that characterize the soil, and H represents the dimensionless soil moisture content.

The van Genuchten equations have a number of desirable attributes. First, the equations describe characteristic curves with plausible shapes throughout the range from zero to high moisture tensions, which include a zero value of soil moisture capacity at zero pressure. Second, the soil moisture content and hydraulic conductivity relations form a consistent pair of relations, which means that the relations as a pair are physically plausible. Third, the relations are adapted to particular soils by fitting only five parameter values (θ_s, θ_r, K_s, α, and n). Two of the parameters are empirical (α and n), but their values can be derived for a particular soil from data on moisture content and soil moisture tension for the soil. Values of α and n used in the simulations are reported in Figure 2.

Moisture flux across a membrane is modeled as being proportional to the difference in head on either surface. The constant of proportionality is termed "leakance." Flux is given by:

$$q_T = C_T \Delta h_T \tag{10}$$

where q_T is the flux per unit length, C_T is the leakance of the membrane, and Δh_T is the head differential across the membrane. The leakance is the sole hydraulic property of membranes, because it is assumed that they do not store moisture. The leakance represents the ability of the membrane to allow soil moisture movement under a unit head differential across the membrane. An impermeable membrane has a leakance value of zero. A permeable membrane has a non-zero leakance value. That non-zero leakance can be the result of the normal installed properties of the membrane or the result of distributed perforations.

Numerical Solution

Equation 1 is solved by the Galerkin finite element method (3). The fundamental idea of the finite element method is to replace the exact continuous solution of the original partial differential equation by an approximate piecewise continuous solution. The piecewise continuous function is described by soil moisture potentials specified at a finite number of discrete points called nodes. Potentials between these points are calculated by using interpolating functions defined over a finite number of subdomains called elements. The interpolating functions will provide an exact representation as the element size approaches zero in the limit. For a finite number of elements and nodes, the approximation will not exactly satisfy Equation 1, and a residual will result. The Galerkin method forces this residual to zero, in an average sense, through selection of coefficients for the interpolating functions.

An interpolating function of the form:

$$h(x,y,t) \approx \bar{h}(x,y,t) = \sum_{i=1}^{n} H_i(t)\phi_i(x,y) \tag{11}$$

is used, where $\bar{h}$ is a series approximation to h,ϕ_i are linearly independent interpolating functions defined over the flow domain Ω, H_i are undetermined coefficients, and n is the number of nodal points.

The Galerkin finite element method yields a system of n ordinary differential equations that can be solved for the n values of $H_i(t)$. The matrix form of the system of equations is:

$$[A]\{H\} + [B]\left\{\frac{dH}{dt}\right\} + \{F\} = 0 \tag{12}$$

where the typical elements of [A], [B], and {F} are:

$$A_{ij} = \int_\Omega (K_{xx}\frac{\partial\phi_i}{\partial x}\frac{\partial\phi_j}{\partial x} + K_{xy}\frac{\partial\phi_i}{\partial x}\frac{\partial\phi_j}{\partial y} + K_{yx}\frac{\partial\phi_i}{\partial y}\frac{\partial\phi_j}{\partial x} + K_{yy}\frac{\partial\phi_i}{\partial y}\frac{\partial\phi_j}{\partial y})d\Omega \tag{13}$$

$$B_{ij} = \int_{\Omega} \left(\frac{d\theta}{dp} + S_s\right)\phi_i\phi_j d\Omega \qquad (14)$$

and

$$F_i = -\int_{S_2} q_B\phi_i dS \qquad (15)$$

The matrices [A] and [B] have the dimensions [nxn] and the vector {F} has the dimensions [nx1].

The matrices [A] and [B] and the vector {F} are commonly referred to by names taken from structural engineering, where the finite element method was first applied. The matrix [A] is referred to as the stiffness matrix, because in structural problems the matrix [A] expresses the stiffness of a structure. From a similar background, the matrix [B] is referred to as the mass matrix, because it expresses the mass of a vibrating structure. Finally, the vector {F} is referred to as the load vector, because in structural problems it expresses the external forces on a structure.

To facilitate the integrations in equations 13 - 15, the interpolating functions are defined piecewise in each element and their union produces global interpolating functions within the flow domain. The elemental interpolating functions are linear and are defined over two-dimensional triangular elements within zones occupied by soils or waste and over one-dimensional linear elements where membranes occur. Triangular elements, which are used to represent soils and soil-like porous media, have three nodes (Figure 3), and yield [3x3] elemental matrices. Linear elements, which are used to represent membranes, have four nodes (Figure 4), and yield [4x4] matrices.

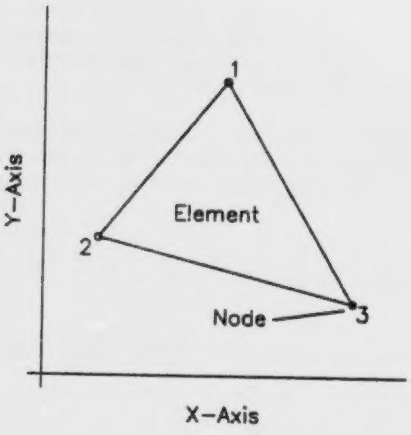

Figure 3. Triangle element representing soils and soil-like porous media.

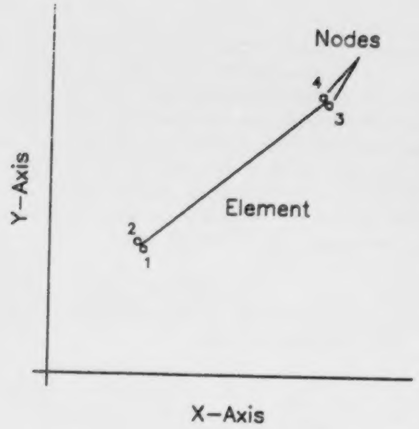

Figure 4. Linear element representing a membrane.

Equations 13 - 15 are performed on an element by element basis, but the results of those integrations are assembled into global matrices. Elemental stiffness and mass matrices are generated, and the results are then transferred to the global stiffness and mass matrices. The global matrices are obtained by summing, for a given node, the contribution to that node from each elemental matrix. This procedure is described by Wang and Anderson (3) for each node in an element and for all elements in the domain Ω.

Equation 12 is discretized in time by an implicit finite difference representation of the time derivative, which leads to a system of algebraic equations for the n coefficients $H_i(t)$ at time t. However, the coefficients of the matrices [A] and [B] depend in part on hydraulic head, and the system of algebraic equations is nonlinear because of the dependence of hydraulic conductivity and soil moisture on head. Fortunately, the nonlinearity introduced by the soil characteristics is not too severe, and a solution of Equation 12 can be obtained by a simple iterative procedure. The iterative procedure is a two step predictor-corrector scheme. In the first iteration, heads at the one-half time step are predicted using soil properties based on heads at the beginning of the time step. Using heads at the one-half time step, soil properties are reevaluated. Then, using these corrected soil properties, heads at the end of the time step are computed.

The mathematical basis described above has been incorporated into the computer program UNSAT2D. The program includes components for data input and for the march of the numerical solution through time. The data input component reads information on the problem geometry, material hydraulic properties, initial conditions, and boundary conditions. The time march component includes an outer time step loop and an inner predictor-corrector loop. The time step loop is repeated for the specified number of time steps in the simulation, and the predictor-corrector loop is repeated twice for each time step.

APPLICATION

To investigate moisture movement at facilities equipped with leachate collection and removal (LCR) and liner systems, a series of computer simulations have been performed.

The focus of analysis in this study is the performance of the LCR and liner systems. Insofar as the function of these systems is to contain hazardous constituents and promptly detect any leaks that should occur, measures of performance include:

- the minimum top liner leak rate that will cause LCR system drains to flow;
- the time required for a given leak to cause drain flow;
- the pattern of drain flow a given leak evokes;
- the leachate collection efficiency expressed as the ratio of LCR system drain flow to top liner flux; and
- the total volume of moisture lost from the facility to the surrounding environment.

The simulated facility is a double-lined surface impoundment with various degrees of top liner failure and different bottom liner designs. The physical system, illustrated in Figure 5, consists of a 300-foot wide by 10-foot deep surface impoundment with 4:1 sideslopes and 2 percent lower slopes.

In the series of simulations discussed in this paper, the LCR system consists of a one-foot thick layer of sand (saturated hydraulic conductivity of 10^{-3} cm/s) and a system of five drains resting on the bottom liner. Figure 2 describes the hydraulic properties of the sand. The drainage layer is bounded above by a flexible membrane liner (FML), which constitutes the top liner. A two-foot thick sludge layer blankets the top liner and is assigned a saturated hydraulic conductivity of 10^{-4} cm/s.

Two types of bottom liners have been simulated. Composite bottom liners consist of an upper FML component underlain by a low-permeability compacted soil component. Non-composite bottom liners lack the upper FML component. The compacted soil layer in the model has a clay texture with a saturated hydraulic conductivity of 10^{-7} cm/s. Hydraulic properties of the clay are described by Figure 2. A static water table exists at a depth of 20 feet, and the surrounding loam-textured soil has a saturated hydraulic conductivity of 10^{-4} cm/s.

The sand drainage layer is assigned an initial soil moisture tension of 0.1 bar (24 percent moisture v/v), and the compacted soil layer is assigned an initial soil moisture tension of 0.33 bar (27 percent moisture v/v). Initial moisture tension in native soil and sludge is hydrostatic with respect to the water table and impounded liquid surface, respectively. Before leakage into the LCR system occurs, the facility is allowed to equilibrate for approximately three years. At the end of this period, leakage across the top liner begins.

The model is bounded by the sludge layer at the top, a ten-foot native soil fringe to the sides, and by three feet of soil below. Boundary conditions are prescribed potential. The boundary condition on the top sludge surface is calculated as the pressure potential with respect to the surface of the impounded liquid. Boundary conditions at the bottom and sides are calculated as the pressure potential with respect to the water table. Because the facility is symmetrical about a vertical centerline, only half the problem is modeled.

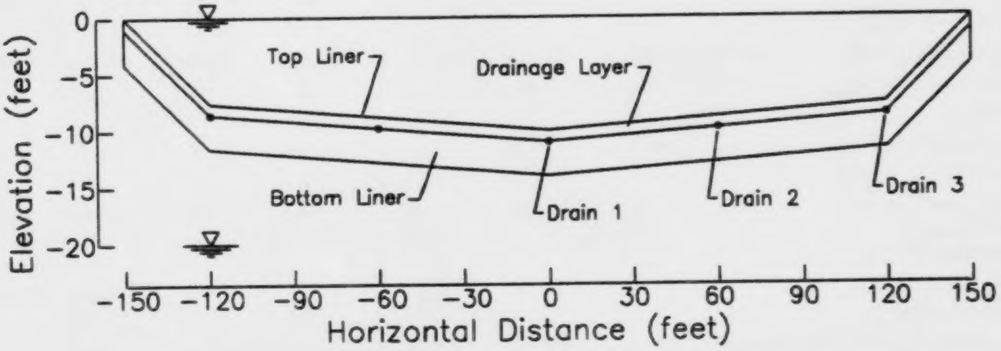

Figure 5. Schematic of the surface impoundment used in the simulations.

Non-composite Bottom Liners

In a set of three simulations, moisture passes into the drainage layer across a uniformly leaky top liner at rates of 14 gallons/acre-day, 95 gallons/acre-day, and 795 gallons/acre-day. These non-composite (NC) bottom liner simulations are identified as NC-14, NC-95, and NC-795, respectively. In each case, the bottom liner is a three-foot thick layer of compacted clay-textured soil. Figure 6 shows the soil moisture potentials that surround each of the drains as functions of time. Negative potentials exist in unsaturated soils and potentials rise towards zero as soils approach saturation. At nonnegative potentials, soils are saturated and drain flow occurs. Summarized results from these simulations are reported in Table 1.

The simulation data suggest that a top liner flux in excess of 95 gallons/acre-day is necessary to achieve saturation and drainage in the LCR system. In simulation NC-95, soil moisture potential at the drains increases over time but stabilizes after six to eight years (Figure 6). Soil moisture potential at the centerline drain (Drain 1) reaches -9 cm at steady state. Drains 2 and 3 do not approach zero potential as closely because their vertical position realtive to Drain 1 causes the equilibrium soil moisture potential around them to be more negative because of their position with respect to the water table. A top liner flux of 95 gallons/acre-day causes soil potentials around drains to approach closely to zero which suggests that this flux is near the threshold leak rate required to cause drain flow in a facility of this design.

In simulation NC-795, drains begin to flow 3.1 months after the top liner leak begins. When steady state conditions are realized after roughly five months, flux across the

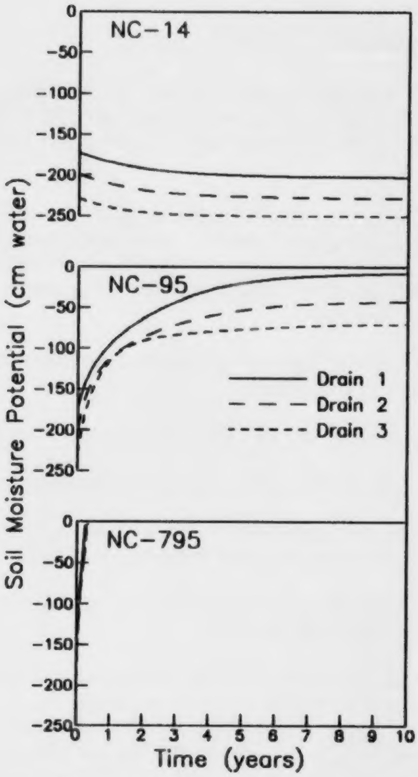

Figure 6. Soil moisture potentials at LCR system drains for non-composite bottom liner simulations.

TABLE 1. LCR/LINER SYSTEM PERFORMANCE SUMMARY

Simulation	NC-14	NC-95	NC-795	NC-795-6	NC-64-6	NC-76-6	C-777	C-60
Top Liner Flux (gallons/acre-day)	14	95	795	795	64	76	777	60
Top Liner Leak Location	Uniform	Uniform	Uniform	Uniform	Uniform	Uniform	Uniform	Sidewall
Bottom Liner Thickness (feet)	3	3	3	6	6	6	3	3
Time to Drain Flow (months)	no flow	no flow	3.1	2.8	no flow	71	1.0	16.5
Steady State Flux into Bottom Liner (gallons/acre-day)	14	95	174	144	64	68	0.002	0.002
Steady State Leachate Collection Efficiency	--	--	0.78	0.82	--	0.11	>0.999	>0.999
Cumulative Loss from Unit after 40 years (gallons/acre)	213,000	1,320,000	2,530,000	2,070,000	875,000	943,000	300	300

bottom liner is 174 gallons/acre-day. Leachate collection efficiency, defined as the ratio of steady state drain flux to steady state top liner flux, is 0.78.

In simulation NC-14, soil moisture potential at the drains declines over time as a result of net moisture movement out of the drainage layer and through the underlying liner (Figure 6). Net drying of the sand layer occurs because it was initially assigned a greater soil water potential than the underlying compacted soil layer. After a period of roughly five years, moisture conditions at the drains stabilize in response to the combined effects of moisture influx from above, unsaturated hydraulic properties of the drainage layer, bottom liner, and native soil, and distance to the water table beneath the facility.

Increasing the thickness of a compacted soil bottom liner from three to six feet does not significantly improve its ability to act as an impermeable barrier to moisture movement. A fourth simulation was identical to NC-795 except that the bottom compacted soil liner was six feet thick rather than three feet thick. Table 1 summarizes results from this simulation, identified as NC-795-6. Increasing liner thickness from three to six feet results in a slight decrease in time to drain flow (3.1 to 2.8 months) and a slight increase in leachate collection efficiency (0.78 to 0.82).

The minimum top liner leak rate necessary to cause drain flow in an LCR system above a six-foot thick compacted soil bottom liner was found to be between 64 and 76 gallons/acre-day. In simulation NC-76-6 (Table 1) a flux of 76 gallons/acre-day across a uniformly leaky top liner causes the centerline drain (Drain 1) to flow after 71 months. Soils at Drains 2 and 3 never reach saturation and never flow. In simulation NC-64-6 (Table 1), a top liner flux of 64 gallons/acre-day is insufficient to cause drain flow.

Composite Bottom Liners

When a composite bottom liner is substituted for a non-composite bottom liner, LCR system effectiveness is greatly improved. Time to drain flow is reduced, minimum top liner flux that will cause drains to flow is reduced, and leachate collection efficiency increases. This improvement is demonstrated by composite (C) bottom liner simulation C-777, in which moisture enters the drainage layer across a uniformly leaky top liner at 777 gallons/acre-day. The bottom liner consists of an FML component above a three-foot thick compacted soil component. The FML component of the bottom liner is allowed to pass moisture at a rate of approximately 0.02 gallons/acre-day, which is a typical rate for vapor phase transport across an intact FML (1). Tabular performance data for C-777 are reported in Table 1, and soil moisture potentials at the drains are shown in Figure 7.

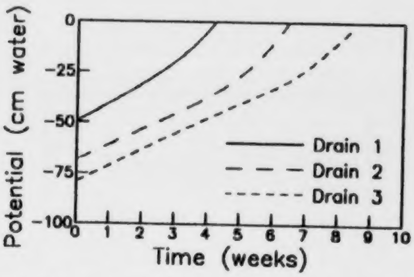

Figure 7. Soil moisture potentials at LCR system drains for simulation C-777.

In simulation C-777, a top liner flux of 777 gallons/acre-day causes drain flow 1.0 month after leakage begins. This delay is a consequence of the absorptive capacity of the granular drainage material. Only when a sufficient volume of moisture is added to the drainage layer will soils around the drains become fully saturated and drain flow begin. Since the FML component of the composite bottom liner allows very little moisture to pass into the bottom liner, virtually all the moisture that leaks into the drainage layer during this period is used to satisfy this absorptive capacity. Because the absorptive capacity of a soil is a function of initial moisture content and moisture characteristic curve (e.g., Figure 2a), the wetting period may be reduced with an initially wetter drainage layer and/or with a coarser drainage material such as coarse sand or pea gravel, for example.

Since a net increase in the moisture content of a drainage layer is possible only when top liner flux exceeds flux into the bottom liner, the bottom liner leak rate defines the minimum detectable top liner leak rate. An LCR/liner system using a composite bottom liner in good condition can be expected to have a bottom liner leak rate of less than 1 gallon/acre-day. Constant wetting of the drainage layer is possible for top liner fluxes greater than this and drain flow will eventually occur. This top liner leak rate is much lower than the approximately 100 gallons/acre-day required to cause drain flow in LCR systems above three-foot thick non-composite bottom liners.

Leachate collection efficiency is greatly improved when composite bottom liners are used. A collection efficiency approaching 1.0 is achieved by simulation C-777, compared with an efficiency of 0.78 achieved by NC-795.

The preceding simulations use uniformly leaky top liners that allow moisture to enter the drainage layer along its entire length. In simulation C-60, the top liner is impermeable except for ten-foot wide sections centered on either sideslope through which moisture enters the drainage layer at a rate of 60 gallons/acre-day. Otherwise, the facility design of C-60 is identical to that of C-777. Table 1 summarizes data from this simulation. Soil moisture potentials at the drains are presented in Figure 8.

Simulation C-60 illustrates the response of an LCR system to a localized top liner leak. As evidenced by the change in soil moisture potential at the drains (Figure 8), moisture that enters the drainage layer on the facility

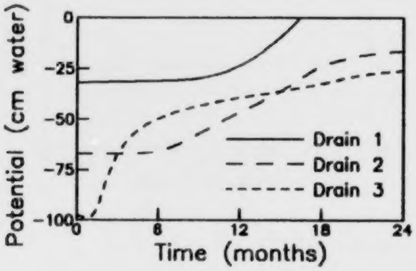

Figure 8. Soil moisture potentials at LCR system drains for simulation C-60.

sideslope travels downslope past Drains 2 and 3 by unsaturated flow and collects in the vicinity of Drain 1 on the facility centerline. Drain 1 eventually flows after 16.5 months. Drains 2 and 3 never flow.

Soil around Drain 3, at the toe of the sideslope, begins to wet almost immediately (Figure 8) in response to the sidewall leak approximately ten feet away. After roughly six months, the influence of the sidewall leak reaches Drain 2 and soil there begins to wet. In eight months, soil around Drain 1 begins to wet and that drain flows 16.5 months after the start of the sidewall leak.

Since drains operated at atmospheric pressure cannot remove unsaturated soil moisture and since they are assumed not to contribute moisture, they exert no influence when soil moisture conditions around them are unsaturated. Only when Drain 1 flows does it affect surrounding soil moisture potentials. Drain flow limits adjacent soil moisture potential to a near-zero value and, as a result, the gradual wetting at the other drains is arrested. Figure 8 shows this effect clearly for Drain 2. Eventually, a steady state condition develops in which all moisture passes Drains 2 and 3 in the unsaturated state and only Drain 1 flows. Under these conditions, increasing the number of drains in the LCR system will have no effect on LCR system performance. At large enough leak rates, however, soil moisture potential in the vicinity of the leak can become positive (fully saturated) and the presence of a drain in this zone of saturation will improve the LCR system performance in two ways: the leak can be detected sooner than if a drain is not located nearby, and information about the location of the leak is provided.

SUMMARY

The computer program UNSAT2D is a useful tool for hydrologic analysis of land storage and disposal facility designs. The model simulates both saturated and unsaturated moisture movement in facilities that may contain flexible membrane liners and leachate detection drains. Application of this model to a range of landfill, surface impoundment, and waste pile designs and operating conditions has provided considerable insight into their hydrologic behavior.

ACKNOWLEDGMENT

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REMEDIATION OF AN INDUSTRIAL DUMP SITE - A CASE HISTORY, PART II

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ABSTRACT

The case history of the design and implementation of a remediation strategy for a hazardous waste disposal site is described. Sludges resulting from treatment of diverse chemical manufacturing effluents had been deposited in an unlined surface impoundment over several decades. "Remediation of an Industrial Dump Site - A Case History," presented at the 12th Annual Research Symposium, described laboratory and pilot-scale investigations of a proposed remedial strategy. The proposed process consists of in-situ alkaline sludge extraction coupled with on-site, sequential aerobic-anaerobic, soil-based microbial destruction of recovered organic contaminants. First year pilot plant results, presented previously, indicated rapid organic species extraction from sludges and greater than 95% destruction of recovered extract TOC. This paper will focus on results from second year pilot plant operation and analyses, which have been carried out on residuals present after extraction and treatment processes.

INTRODUCTION

Site Description

Over a period of several decades, industrial waste sludges were landfilled in an unlined surface impoundment. During the period of operation, the compositions and rates of depositions of sludges varied greatly. Primary and secondary sludges were deposited. The primary sludges were lime-neutralized inorganic matter, including neutralization wastes, spent catalysts, and solid residues from diverse chemical manufacturing operations. The secondary sludges were biomass from aerobic treatment of aqueous effluent from the same manufacturing activities.

The resulting 4.1 acre site contains approximately 30,000 cubic yards (yd^3) of sludge. Two principal layers are found within the fill material. The first layer of approximately 15,000 yd^3 of secondary sludges deposited over a ten-year period, prior to 1967. In response to complaints from local residents about obnoxious odors, lime was applied to the secondary sludge. Subsequently, the limed sludge was covered with clean fill and plastic sheeting. The second layer consists of approximately 5,000 yd^3 of primary sludge that was transferred to the site from another lagoon. This sludge was deposited over the layers of fill and plastic sheeting covering the secondary sludges. Mounds of shale fill were placed over the primary sludge to minimize odor problems. This gave rise to approximately 10,000 yd^3 of contaminated fill material. At present, the physical state of the sludges ranges from solid to gelatinous. Leachate from the sludges can impact local groundwater resources. Detailed descriptions of the leachate and sludge characteristics have been presented previously (1).

Pilot Plant Description

Lagoon clean-up is viewed as two interrelated problems. The first problem is the extractive removal of contaminants from the lagoon without major excavation. The second problem is treatment of the extract stream containing the stripped contaminants, which include organic and inorganic species. A research program was designed to evaluate several treatment options for the lagoon. Elements of this program included forced extraction of representative sludge samples and laboratory evaluation of aerobic (secondary) mixed microbial treatment and sequential aerobic/anaerobic soil-based microbial treatment of naturally occurring leachate and forced extracts (2,3,4).

The laboratory program led to the design of a pilot plant incorporating the most promising renovation strategy. The pilot plant employed in-situ extraction of sludge deposits with aqueous sodium hydroxide solution (pH between 9 and 13). (Sodium hydroxide (0.05N) was shown (1,2,5) to be a very effective extractant for this lagoon sludge; significantly different sludges may require other extractants). Recovered extract was treated on-site using a soil-based, mixed microbial treatment system. The pilot system was designed to consist of several sequential process steps. A simplified process flow diagram is presented in Figure 1; additional detail is available (1,5). The first process step was extraction of sludges present in a representative section of the lagoon. Sodium hydroxide solution was mixed (Tank 1) and injected into the sludges or applied to the surface of the extraction bed. Extract was recovered from the extraction bed using two wells and collected in a process tank (Tank 2).

The second process step was the adjustment of pH, dilution if necessary, and addition of nutrients to extract stored in Tank 2. This occurred continously in a baffled process tank (Tank 3). The third process step was treatment of the modified extract (effluent from Tank 3) in an aerobic/anaerobic bioreactor. Treatment occurred in a lined soil bed in which an aerobic microbial population was maintained in the upper region and an anaerobic microbial population was maintained in the lower region. Extract applied to the surface of the treatment

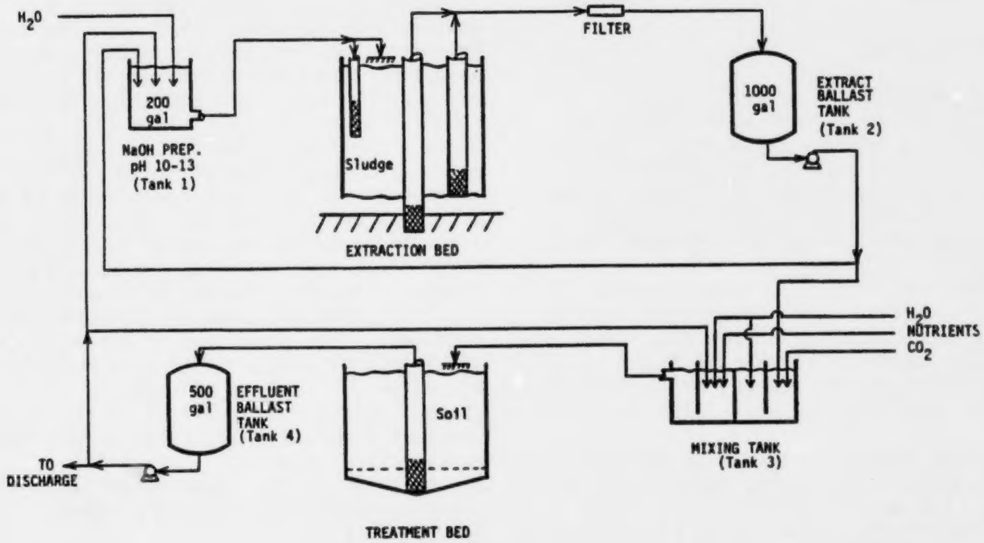

Figure 1. Simplfied process flow diagram.

bed percolated through the soil column where organic contaminants were biodegraded. Effluent from the treatment bed was recovered through a screened well and pumped into a storage tank (Tank 4) prior to recycle or discharge.

Operation of the pilot plant commenced in July 1985 and continued until freezing conditions necessitated a winter shutdown. During 1985, extraction bed effluent pH, total organic carbon (TOC), and total dissolved solids (TDS) were initially approximately 10, 11,000 mg/l, and 28,000 mg/l, respectively. Recovered extract pH initially declined as previously applied lime was extracted, and then increased to 9.5, in response to addition of sodium hydroxide extractant. Extract TOC and TDS both declined during 130 days of operation to approximately 4,000 mg/l and 8,000 mg/l, respectively. Influent TOC to the treatment bed was controlled during prolonged intervals to 1000 mg/l and 2000 mg/l. Integrated TOC reduction for the entire 1985 period of operation was greater than 95% on a mass basis. Steady state TOC reduction, after microbial population development, was greater than 98%.

PILOT PLANT OPERATION DURING 1986

Extraction Bed Results

Completion of pilot plant repairs to correct cold weather damage resulted in full operation start up for the second operating season in June 1986. During 1986, extraction bed effluent pH, TOC and TDS were intially approximately 9.7, 6,000 mg/l, and 13,000 mg/l, respectively. Extract pH remained generally between 9.4 and 9.8 during operation, while extract TOC and TDS declined rapidly after 40 days of operation. Extract TOC and TDS were approximately 2,200 mg/l and 7,500 mg/l, respectively. The TOC response of recovered extract is presented in Figure 2. The initially elevated extract

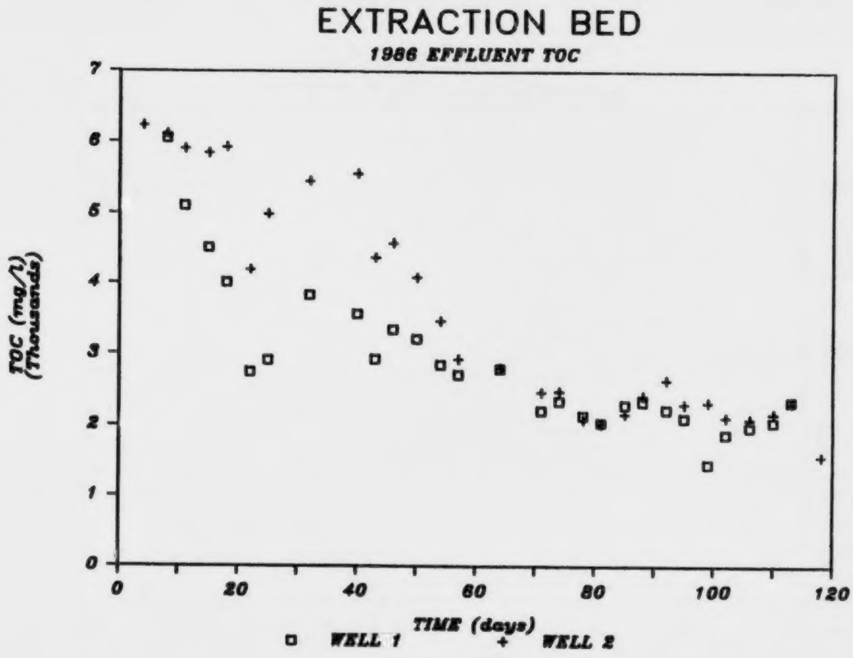

Figure 2.

concentrations, relative to 1985 results, are attributed to the extended extract-sludge contact period during the winter. The apparent response delay during 1986 was between 40 and 50 days. Average hydraulic flux through the extraction bed during 1986 was 8.6 l/m^{2}day, as compared to 3.7 l/m^{2}day for 1985.

Several physical changes were apparent in the extraction bed during operation. Extended periods of extraction during 1985 and 1986 resulted in settlement of the sludges within the extraction bed of between 0.5 and 1.0 ft. In addition, as extraction progressed, the surficial sludges appeared to become more friable. This observation was further supported by increasing sludge permeability during operation.

Treatment Bed Results

Influent and effluent volumetric fluxes for the treatment bed varied between 3.6 and 9.4 l/m^{2}day, depending on mode of operation, as compared to between 15.1 and 17.9 l/m^{2}day during 1985.

Throughout operation, influent pH was targeted to be maintained between 7.5 and 8.0 although occasional power supply interruptions resulted in brief periods of influent pH between 8.0 and 8.5. Effluent pH remained between 6.3 and 6.8 throughout operation.

Influent and effluent TOC data for the treatment bed are presented in Figure 3. Influent TOC was maintained at approximately 1,200 mg/l for 30 days following a brief start up with a glucose/nutrient medium. Note, no microbial inoculum was used for startup in 1986. After day 40 of operation, the influent TOC to the treatment bed was adjusted to between 2,000 and 2,500 mg/l. In contrast to the microbial acclimation period observed during 1985, no substantial microbial acclimation period was apparent from the effluent TOC responses. Increased effluent TOC after day 70 was a delayed response to increased influent TOC starting day 40. Integrated TOC reduction over the entire period of operation was greater than 99%, on a mass basis. Typical TOC treatment capacity ranged from 7 to 22 g/m^{2}day, which was in close agreement with laboratory soil column data (6).

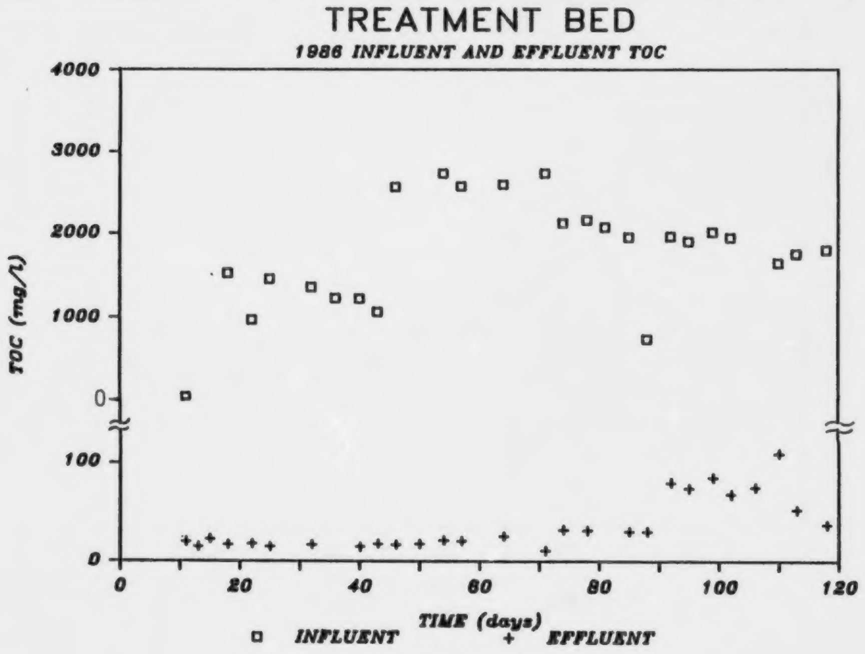

Figure 3.

EXTRACTION BED RESIDUALS ANALYSIS

Extraction of Split-Spoon Core Samples

At the conclusion of operation of the extraction bed, split-spoon sampling was carried out to retrieve sludge samples for laboratory analysis. Four cores were obtained at the conclusion of operation in 1985 and two cores were obtained at the conclusion of operation in 1986. Core locations within the extraction bed are indicated in Figure 4. The samples retrieved were segregated by core number and sampling depth. Each split spoon sample retrieved represented a two foot deep core section. A description of sludge composition as a function of depth is presented in Table 1.

Sixteen of the core samples obtained in 1986 were extracted in the laboratory with 0.05N sodium hydroxide solution to evaluate the uniformity and effectiveness of the extraction bed operation. Each core sample tested was homogenized

TABLE 1. EXTRACTION BED CORE SAMPLE DESCRIPTIONS

Depth (ft)	Sludge Description
0-2	Primary
2-4	Primary
4-6	Primary
6-8	Primary
8-10	Primary with some secondary
10-12	Even mixture of primary and secondary
12-14	Secondary
14-16	Secondary with some clay
16-18	Secondary with some clay
18-20	Even mixture of secondary and clay
20-22	Clay with some secondary

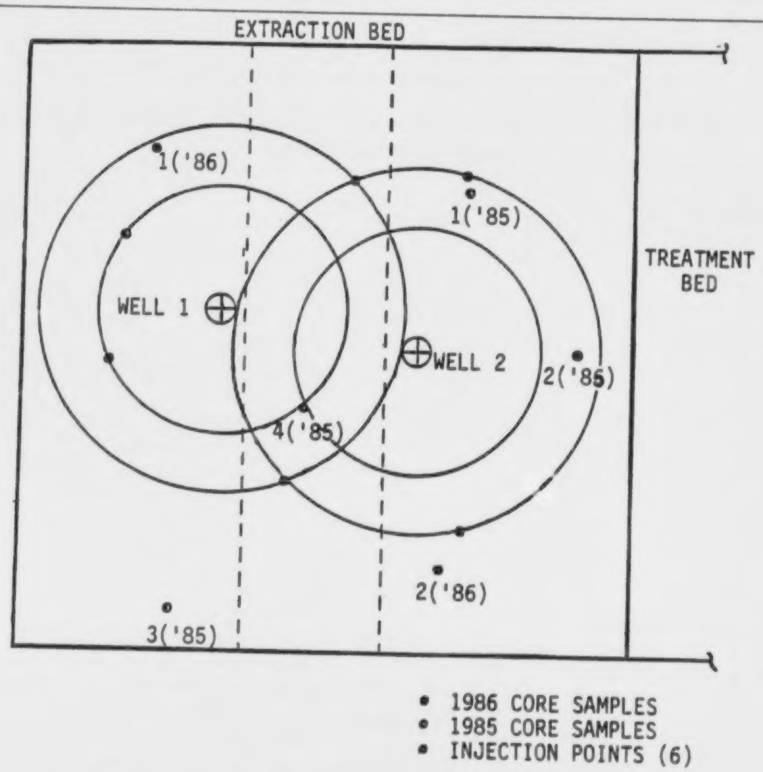

Figure 4. Extraction bed core locations.

individually and two 10-g aliquots were shaken with 100 ml of the sodium hydroxide extractant for 40 hours on a rotary shaker. The resulting mixture was separated into solid and liquid phases through centrifugation and filtration. Recovered extract was analyzed for TOC; results are presented in Figure 5. The extract TOC data indicates a pocket of inefficiently extracted sludges between depths of 6 and 12 ft, while sludges present outside of that pocket were extracted fairly thoroughly. Review of previously obtained information indicated that plastic sheeting was present at depths of approximately 4 and 12 ft, while injection points were screened at depths between 11 and 13 ft. Although plastic sheeting was pierced using a rod at regular intervals, pockets of irregular hydraulic flow persisted. This indicates the necessity of careful placement of injection points during scale-up.

In addition to extractable TOC analysis, volatile solids content (weight loss upon ignition at 550 C from sludge previously dried at 105 C for 24 hr) was determined for each homogenized sludge sample (7). Results of analysis carried out in 1984 on untreated primary and secondary sludge samples was compared to results obtained from Core 1 (1986) at depths of 4-6 ft and 12-14 ft. These particular samples were considered representative of primary and secondary sludges before and after effective in-situ extraction. The comparison is presented in Table 2.

Neutralization and Leachability of Final Residuals

Laboratory experiments were carried out to determine the quantity of acid required to neutralize the solid residuals present after in-situ extraction was completed and assess the leachability of neutralized residuals. Thus, a possible process end-state was investigated. The quantity of acid required was determined by titration of 10-g aliquots of the homogenized core samples, shaken in 100 ml of distilled water and titrated with 1.0 N sulfuric acid. Samples were shaken on a

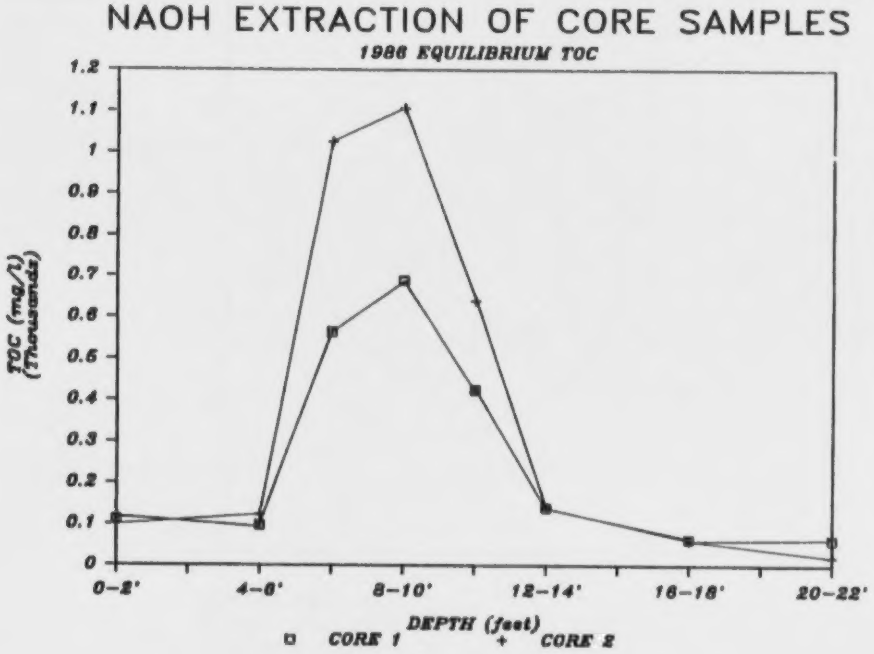

Figure 5.

rotary shaker until a constant pH was obtained after each addition of titrant (approximately 40 hrs). Samples were considered neutralized after an equilibrium pH of 5.0 was achieved. Solid and liquid phases of the resultant neutralized mixture were separated by centrifugation and filtration. The recovered aqueous phase subsequently was assayed for TOC. The number of equivalents of acid required to neutralize each titration mixture and the resultant equilibrium TOCs are reported in Figure 6. The number of equivilents of acid required to neutralize sludge samples correlated closely with the amount of leachable residual TOC. In addition, TOC leachability from core samples was approximately ten times less for neutralized samples than for samples similarly extracted with 0.05 N sodium hydroxide solution (Figure 5).

TABLE 2. SLUDGE CHARACTERISTICS BEFORE & AFTER IN-SITU EXTRACTION

	Before (1984) (mg/g)	After (1986) (mg/g)	Change (%)
TOC Extracted with 0.05 N NaOH:			
Primary	3.2	1.1	65
Secondary	8.7	1.4	84
Volatile Solids:			
Primary	200	45	78
Secondary	320	22	93

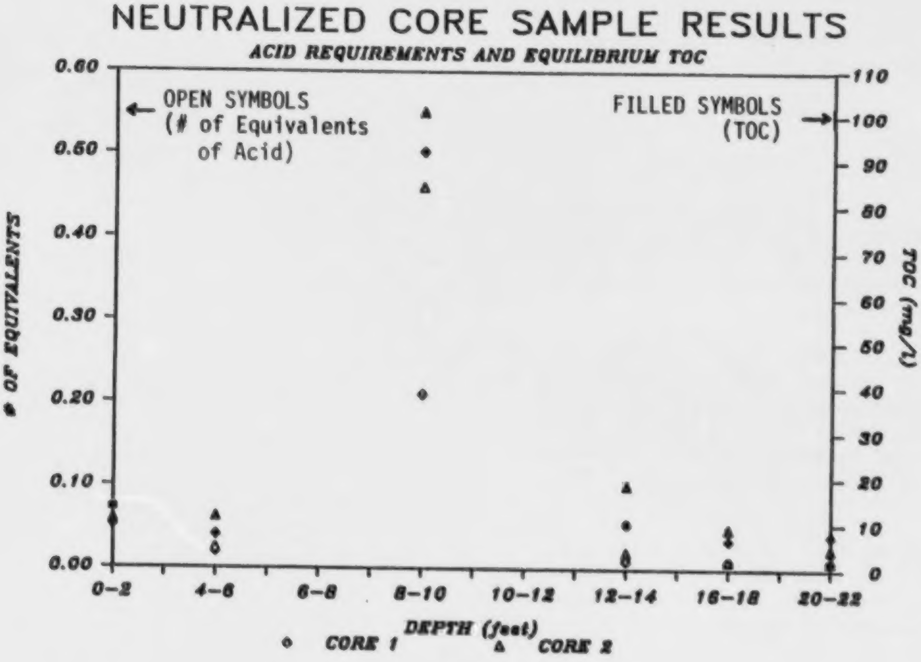

Figure 6.

CONCLUSIONS

Operation of a large-scale pilot plant on-site at an industrial sludge impoundment successfully demonstrated the feasibility of in-situ alkaline extraction followed by on-site soil-based microbial treatment as a renovation process, for this case. Extraction uniformity was influenced heavily by extractant injection locations and local hydraulics. Solid residuals present after in-situ sludge extraction can be neutralized through addition of limited quantities of mineral acid. Neutralized residuals leach greatly reduced amounts of TOC. In addition, soil-based sequential aerobic/anaerobic microbial treatment removed greater than 99% of the TOC, on a mass basis, present in the recovered extract.

ACKNOWLEGEMENT AND DISCLAIMER

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CAPILLARITY AND ANISOTROPY EFFECTS ON GROUND-WATER FLOW TO EXCAVATION

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ABSTRACT

In a hazardous waste disposal facility located in a saturated soil, the local water table and the capillary fringe zone are modified by the presence of the facility. In this paper, a conformal mapping solution to the accompanying ground-water flow is discussed. The flow net around an excavation is calculated and displayed in terms of the capillarity, local geometry and flow properties.

Capillarity can significantly influence net flow into an excavation; typical values can cause net flow to be 10 to 20 percent higher than predicted without capillarity. Anisotropic behavior can also be important. It is shown that anisotropy favoring horizontal flow can greatly alter the flow net and the total flow.

INTRODUCTION

There is increasing interest in the possibilities of siting hazardous waste disposal facilities in locations at which the water table (or the tension-saturated zone immediately above) is near the ground surface (1, 2). This situation is normal in saturated low-permeability soils which exist at various locations of the country but which predominate in the eastern United States because of higher rainfalls and local geologic conditions.

A disposal facility so located would be beneath the water table, and thus would influence the local flow dynamics, including the water table and the capillary fringe (3). The prediction of these effects is the problem of concern in this paper. Also considered are the effects of anisotropy on the local ground water flow.

The problem to be addressed is presented schematically in Figure 1, which shows a disposal facility, idealized as a two-dimensional rectangular excavation, sited such that its lower surface is beneath the normal water table. As in a well, there is a tendency for ground water to flow into the excavation. A complicating factor, however, is capillary attraction, which draws fluid into the soil interstices and creates a zone of negative pressure, the capillary fringe or tension-saturated zone.

Figure 1 shows the excavation, the flow profile into the excavation including lines of constant potential and stream function, the free surface (immediately beneath which $P = -H_c$), and the water table (along which $P = 0$). (A

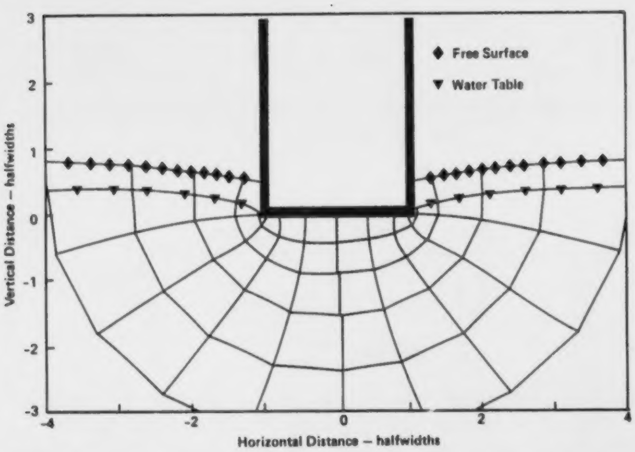

Figure 1. Schematic of disposal facility slightly below normal water table.

List of Symbols is provided at the end of the paper).

In the capillary fringe, the region between the water table and free surface, the physical picture is that of individual granules whose interstices contain no significant vapor bubbles (4, 5). This zone is normally referred to as the tension-saturated zone or the negative pressure zone.

Above the top of the capillary fringe, the physical appearance is that of individual granules whose interstices are filled primarily with vapor or gas bubbles (4, 5). This region is referred to as the unsaturated zone and its moisture content normally decreases with elevation or increases with depth.

APPROACH

Our purpose is to assess the effects of the capillary fringe on the fluid flow patterns in the neighborhood of the excavation. This is done by formulating and solving the equations of motion for the flow field with the equilibrium capillary rise, H_C, as an adjustable parameter. Comparative analysis of the solutions for various values of the equilibrium rise should reveal and quantify its effects.

Classical potential theory (6), which applies here, and in which the flow is proportional to the gradient of some potential, provides a relatively easily visualizable and familiar representation of the flow field in the form of the flow net. This net is comprised of lines of constant potential, say ϕ, and orthogonal, or perpendicular, lines of constant stream function, say ψ. The lines of constant stream function, or stream lines, represent particle tracks in steady flow; hence no fluid flows across these lines. Any two such lines form a stream tube, through which the total flow is constant.

A particularly simple flow net is shown in the rectangle in the center of Figure 2. In this flow net, the horizontal lines represent lines of constant potential, ϕ, and the vertical lines represent stream lines or lines of constant stream function, ψ. Thus the flow field represented by this rectangle is uniform flow from high potential to low potential, thus uniformly upward.

Imagine now that the lines of constant potential and flow lines in this rectangle

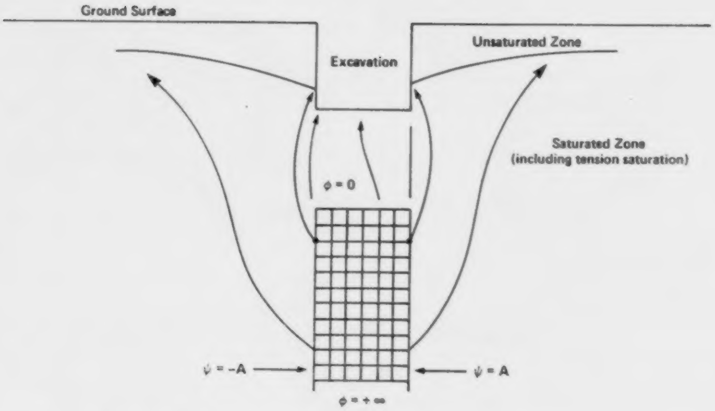

Figure 2. Schematic of overview mapping.

(Figure 2) are drawn on an infinitely stretchable thin sheet of rubber. Imagine moreover that this rectangular piece of rubber is positioned and deformed as indicated in the figure so that the outside edges correspond as indicated to the centerline of the excavation, the bottom of the pit, and the free surface. If this stretching is done in such a way that angles are preserved, e.g., conformally, then the resulting curvilinear network comprising the (now deformed) lines of constant potential and constant stream function represents a new flow field, the one sought in this study.

Conformal mapping is a mathematical formalism for accomplishing this stretching. In a typical application, a simple flow configuration (the rectangle) is mapped onto a more complicated geometry (the disposal facility) in such a way that the important mathematical features of the flow net are preserved and the resulting curvilinear flow net is a theoretically accurate representation of the flow field in the more complex geometry. The mathematical formalisms are developed elsewhere (7) and solutions are presented from which the behavior at various values of the capillarity can be compared.

SCALING

In this analysis, all distances have been scaled to the excavation half-width, including the equilibrium capillary rise, H_C. Moreover, all velocities have been scaled to the free-drain velocity, which is superficial velocity resulting from a head gradient of unity (1 ft/ft). Thus, a value of A = 1 would correspond to a flow velocity given by

$$V_0 \equiv \frac{Kg}{\nu}$$

operating over the area of the excavation bottom.

For present purposes, it is adequate to consider the quantity A as simply a measure of relative flow into the excavation.

ANALYSIS OF CAPILLARITY

Computed results illustrating the effects of capillarity are shown in Figures 1 and 3. Figure 1, in addition to serving as a schematic of the problem, is also a flow map included to establish axes, scales, and formats for Figure 3. The latter figure represents a compilation

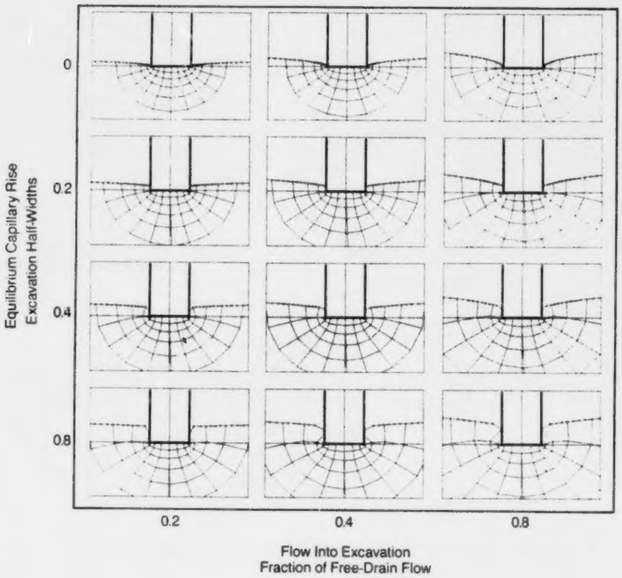

Figure 3. The effects of total flow into the excavation and the equilibrium capillary rise on the resulting net rise.

of cases, plotted to the same scale as in Figure 1, but omitting, for convenience, the location of the water table, and reduced so as to fit on the same sheet for comparative purposes.

Referring to Figure 3, moving to the right increases A, the relative flow into the excavation. The second and third columns of figures represent progressively lower positions of the excavation base with respect to the water table, hence, higher flows into the facility.

Moving downward in Figure 3 corresponds to increasing the equilibrium capillary rise, H_c. An interesting feature is the extent to which the elevation of the free surface at the excavation wall is dependent upon A, the relative flow. The point of intersection is bounded from below by the equilibrium capillary rise and increases with flow, A.

The effects of capillarity can be further quantified as shown in Figures 4 and 5. To generate these figures, the hydraulic gradient in the vicinity of the excavation was first estimated for each case in Figure 3. This was done by first estimating the gradient as the slope of the line segment connecting the corner of the excavation to the location of the water table 4.5 half-widths away. Crossplotting the resulting information as flow vs. gradient with capillarity as a parameter gives Figure 4. Expressing flow as a percent increase over the no capillarity case gives Figure 5.

The analysis shows that capillarity does, indeed, increase the net flow into the excavation by small, but significant amounts, with the increase being roughly proportional to the equilibrium capillary rise.

Figures 4 and 5 can be utilized to estimate the flow into the excavation. First, one estimates the local gradient of the water table and then, with Figure 4, determines the no-capillarity flow. Next, one estimates the capillarity from grain size or by some other method. Figure 5 is then used to predict the net increase in the flow.

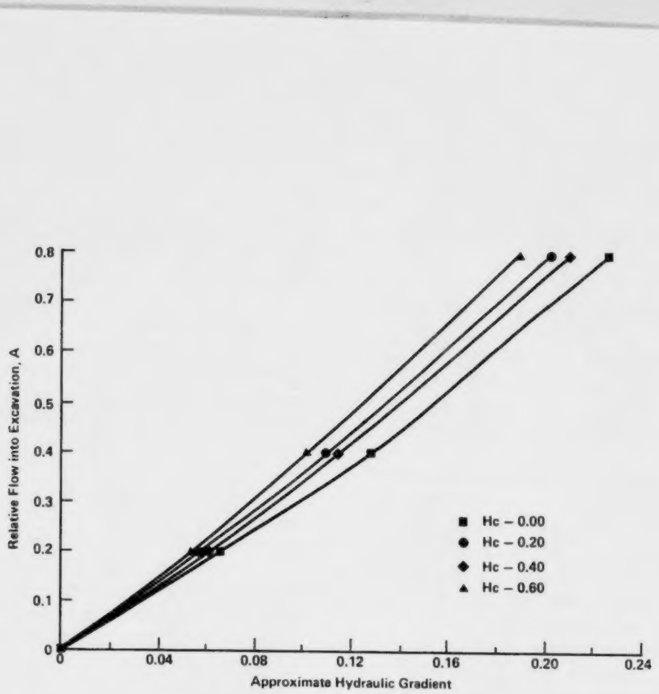

Figure 4. Effect of hydraulic gradient on relative flow.

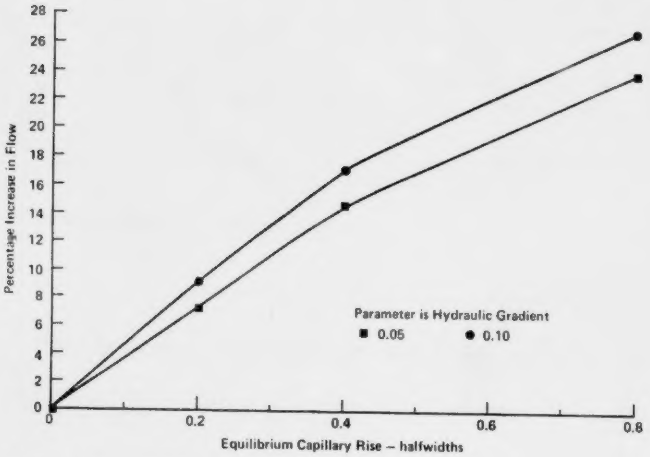

Figure 5. Effect of capillarity on relative flow.

Physically, one can reason that flow increases with capillarity because the capillary rise provides more lateral area for flow to cross for a fixed hydraulic gradient.

ANALYSIS OF ANISOTROPY

Soils can be quite anisotropic, with horizontal permeabilities exceeding values by several orders of magnitude (3).

Omitting mathematical details, anisotropic flow profiles cases have been computed with values of K_x/K_y from 1 to 64. Graphical results from these calculations are summarized in Figures 1 and 6.

Figure 1, as before, establishes axes, scales and formats for Figure 6. The latter figure represents a compilation of cases, plotted to the same scale as that used in Figure 1, reduced so as to fit on the same sheet for comparative purposes.

Referring to Figure 6, moving downward increases the capillarity, H_c. Moving to the right corresponds to increasing the anisotropy, specifically the x-direction permeability relative to that in the y-direction. The results are as one would expect, though the magnitude is surprisingly large. Further analysis follows in Figure 7 which was generated from the computed results for the special case of intermediate capillarity (H_c = 0.4) by the following procedure.

Approximate hydraulic gradients were estimated as the slopes of the line segments connecting the corner of the excavation to the water table 4.5 half-widths way. Relative flow from (into) the excavation, the A values, were then plotted against these hydraulic gradients with the permeability ratio as a parameter.

Intuitively, it is expected that increasing the horizontal permeability while holding the vertical permeability constant would have the effect of increasing the flow from (into) the excavation for a given hydraulic gradient. The figure shows that this is indeed the case, quite dramatically. Consider a hydraulic gradient of 0.1. Increasing the permeability ratio fourfold, from 1 to 4, results in an approximate threefold increase in flow into the excavation, from $A \approx 0.5$ to $A \approx 1.5$. Another fourfold increase in the permeability ratio (to 16) results in an approximate fourfold increase in flow, to $A \approx 6$. Still another fourfold increase in the permeability ratio (to 64) gives quite a dramatic increase in the flow, from about 6 to much greater than 32.

The following generalized rule-of-thumb seems to apply: In the two-dimensional approximation, the groundwater flow from (into) an excavation

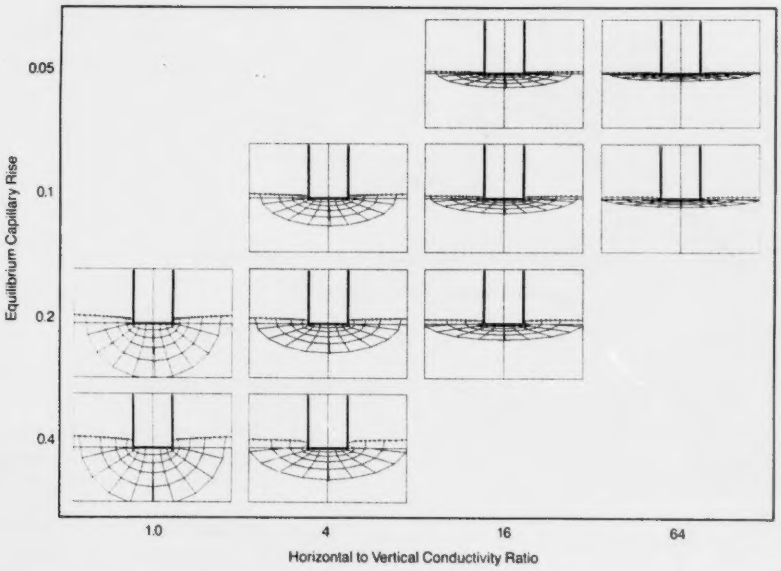
0.05
0.1
0.2
0.4
Equilibrium Capillary Rise
1.0
4
16
64
Horizontal to Vertical Conductivity Ratio

Figure 6. Effect of anisotropy on flow map.

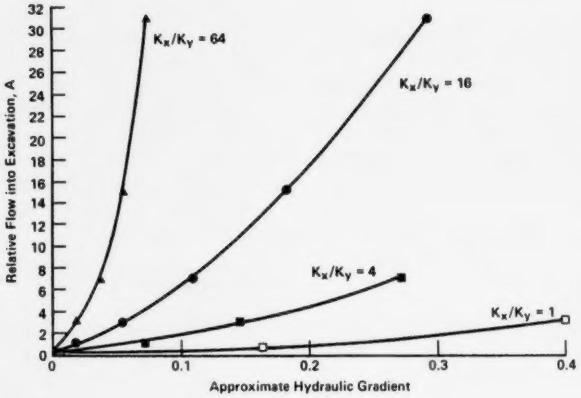

Figure 7. Effect of anisotropy on flow into excavation.

approximately doubles for every doubling of K_x with constant K_y. The effect is stronger at large values of the permeability ratio, e.g., for $K_x/K_y > 16$.

PRACTICAL IMPLICATIONS

Fine-textured soils, e.g., clays have capillary radii in the range of 10^{-4} to 10^{-5} centimeters. Corresponding values for the free-drain velocity, v_0, are in the range of 5×10^{-6} to 5×10^{-8} cm/sec (1 to 0.001 gal/day-ft^2). Moreover, equilibrium capillary rise values for such soils can exceed 50 ft.

For illustrative purposes, assume a soil with free-drain velocity of 1×10^{-6} cm/sec (0.2 gal/day-ft^2). Assume moreover that one is considering the ground-water flow into a long trench-like disposal facility whose width is 100 ft which is located in a soil exhibiting an equilibrium capillary rise of 25 ft. Then the equilibrium capillary rise is 0.5 excavation half-widths. If, moreover, the local hydraulic gradient in the vicinity of the excavation is 0.05, then, from Figure 4, the relative flow into the excavation in the absence of capillarity is about 0.14. Hence the estimated total flow is 0.14 x 0.2 gal/day-ft^2, or 0.028 gal/day-ft^2.

What effect would one anticipate from including capillarity? From Figure 5, at an equilibrium capillarity rise of 0.5 half-widths, one would expect the flow into the excavation to be almost 20 percent higher than estimated for no capillarity.

CONCLUSIONS

A method has been demonstrated for the formulation and solution of ground-water flow problems involving a free surface, e.g., a conceptual interface between liquid-filled interstices and vapor-filled interstices. This method has been applied to predict the effects of capillarity and anisotropy on flow patterns in the vicinity of a disposal facility located beneath the local water table.

The solution to the problem for zero capillarity provides a baseline estimate of the flow into the excavation in terms of the local hydraulic gradient.

The effect of capillarity is to draw fluid vertically into the soil interstices and thence to open the area through which fluid can flow into the excavation. Capillarity thus causes the flow into an excavation to increase over the no capillarity case; the magnitude of the increase can be on the order of 10 to 20 percent of the total flow and is higher for higher hydraulic gradients.

Soils frequently exhibit anisotropic flow behavior in that the horizontal hydraulic conductivity is greater than the vertical. This phenomenon can increase the net flow substantially at a given hydraulic gradient as a result of the more open horizontal flow path for liquid motion.

LIST OF SYMBOLS

A = Value of stream function at lower right corner of excavation, hence a measure of flow volume to (from) excavation, L.

g = Gravitational acceleration L/T^{-2}

H_c = Equilibrium height of capillary rise above water table.

L = Heterogeneity half-length, L.

K, K_x, K_y = Permeability, permeability components, L^2

P = Manometer pressure, L.

x, y = Horizontal and vertical position coordinates, L.

α = $(K_y / K_x)^{1/2}$

ν = Kinematic viscosity, L^2/T.

ρ = Bulk mass density of fluid, M/L^3 .

ϕ = Piezometric potential, P + y, L.

ψ = Stream function, L.

ACKNOWLEDGMENTS

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PATHWAYS FOR THE REMOVAL OF VOLATILE ORGANICS FROM SURFACE IMPOUNDMENTS

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ABSTRACT

A series of surface impoundments have been investigated to determine the significance of biological oxidation as a major pathway for volatile organic removal. Measurements of the volatile organic concentrations, pH, and dissolved oxygen have been taken from active surface impoundments. Wastewater was removed from selected impoundments, and the rate of oxygen uptake and the compound specific fate of the volatiles was evaluated in the laboratory under both anaerobic and aerobic conditions. A biocide was used to evaluate the significance of biological activity relative to chemical reactions. The results indicated that biological activity is common in surface impoundments. The biological removal of specific components at one impoundment was low relative to the anticipated volatilization rates.

INTRODUCTION

The United States Environmental Protection Agency is developing regulations to control the emissions of volatile organics (VO) from hazardous waste treatment, storage, and disposal facilities. Facultative lagoon systems present a potential source of emissions of this type as they provide an opportunity for mass transfer of VO from the aqueous phase to the atmosphere. Properly designed and operated biological wastewater treatment systems protect water quality by removing organic chemicals from wastewater prior to discharge; the actual fate (biodegraded, transferred to the air, or removed in a separate sludge stream) of this material is uncertain. Visits to three non-aerated wastewater management facilities were made to determine the composition of wastewater in the lagoon and the potential for biodegradation and air emissions. (1, 2, 3)

SITE DESCRIPTIONS

Description of Site A

Site A produces aldehydes, glycols, glycol ethers, nitriles, esters, and other products. Wastewater and runoff are collected at different points within the manufacturing area of the plant. The wastewater flows to a series of seven oxidation basins. Some of the effluent from the basins is pumped to a series of four large unlined facultative basins prior to discharge. Wastewater samples were collected from the first facultative basin (60 acres in area). The discharge permit application for Site A includes the following information about the long-term average, final effluent: BOD, 21 mg/L; COD, 384 mg/L; TOC, 127 mg/L; TSS, 43 mg/L; methylene chloride, 18 μg/L; acenaphthylene, 10 μg/L; bis (2-ethyl hexyl) phthalate, 24 μg/L; naphthalene, 4 μg/L. (1)

Description of Site B

Site B has two adjacent facilities (a refinery and a lube oil plant), and each facility has its own wastewater treatment system. Each wastewater treatment system contains a RCRA-regulated polishing pond near the end of the system. Wastewater samples were collected from each of these polishing ponds for chemical analysis and biological activity testing. In June 1986, upstream from the polishing pond, the wastewater contained 82.7 mg/L COD, 33.7 mg/L TSS, and 0.9 mg/L phenols. (2)

Description of Site C

Site C is a commercial waste facility which treats dilute aqueous waste. The following four lagoons were sampled: Lagoon B, an evaporation pond; Lagoon C, an evaporation pond which receives the overflow from B; Lagoon D, a holding pond; and Lagoon E, a solids settling pond. Samples were taken from the southeast corner and the west end of Lagoon B; only one sampling location was employed in Lagoons C, D, and E. The wastewater at Site C contains a variety of dilute (<20 ppm) organic compounds. (3)

TEST PROCEDURES AND RESULTS

Samples for chemical analysis were collected in one liter amber glass bottles with Teflon-lined screw caps and in 40 ml zero headspace septum bottles. The samples were transported on ice and refrigerated until analyzed. Aside from refrigeration, the samples were not preserved.

At the chemical analysis sampling points, additional samples were obtained for biodegradation rate studies. Wastewater was pumped into five gallon Nalgene containers and shipped to RTI without refrigeration or preservation.

Dissolved oxygen (DO) measurements were made at different depths at the sampling points using a YSI Model 54A dissolved oxygen meter calibrated against saturated air. The pH of the wastewater at each sampling point was determined using short range pH paper.

DO Profile Results

The results of the DO profile measurements are presented in Figure 1. At Site A the DO was greater than saturated except for the bottom of the lagoon. A high concentration of algae in the upper level of the lagoon in combination with the bright sunlight produced super-saturated conditions throughout much of the water. This also is the likely cause for the high pH (approximately 9) as carbon dioxide was removed from the water photosynthetically.

The DO concentration in the refinery polishing pond at Site B was about 8 mg/L independent of liquid depth; the pH was approximately 7. The DO concentration in the lube oil polishing pond at Site B was about 3 mg/L independent of liquid depth; the pH was approximately 7.

All lagoons at Site C had DO concentrations of less than 1.0 mg/L indicating that the lagoons were primarily anaerobic. All of the wastewater collected except from Lagoon E, had a pH of 8-8.5; Lagoon E wastewater had a pH of approximately 13.

Analytical Results

The wastewater samples at Sites A and B were analyzed for volatile organics using EPA Method 624 for purgeables and EPA Method 625 for base/neutral and acid extractables. None of the Method 624 or 625 compounds were present above detection limits in the lagoons.

Samples from Site C were analyzed for specific volatile organics using EPA Method 624 for purgeables and EPA Method 625 for base/neutral and acid extractables. Acetone was present at concentrations of 1.6, 0.05, 2.8, and 16 ppm for Lagoons B, C, D, and E, respectively. Lagoons D and E also contained over 10 ppm methylene chloride, and approximately 1 ppm 1,1,1-trichloroethane, Freon 113, toluene, and total xylenes. No other VO were detected in Lagoons B and C.

Microorganisms

The presence of microorganisms in the wastewater at Site A was initially confirmed by microscopy studies. Several different microorganisms were observed using wet drop slides. These include:

coccoid blue-green algai (Phylum Cyanophyta, anacystis sp.); protozoans (both flagelates and cilliates, numerous species); and green algae (particularly arthrospira).

Site B also contained microorganisms. Several different microorganisms were observed using wet drop slides. These include: protozoans (both flagelates and cilliates, numerous species); and green algae (particularly arthrospira).

The wastewater from Site C contained no motile microorganisms that were observed using wet drop slides. Wastewater samples taken from two locations in Lagoon B appeared to have agglomerations of coccoid blue-green algae. The abundance of inorganic solids, however, especially in the Lagoon D sample, hindered the wet drop slide studies. Both filamentous and nonfilamentous bacteria were observed using Gram-stained slides of Lagoon B, C, and D samples. Both gram-positive bacteria (stained purple) and gram-negative bacteria (stained red) were observed. No cell cultures were grown to further characterize the bacteria.

Aerobic Biological Testing

The first experiment to measure the oxygen consumption rate of the microorganisms measured the dissolved oxygen (DO) depletion rate. The procedure employed was as follows. A wide mouth, amber glass, pint bottle was filled with the wastewater sample and allowed to come to thermal equilibrium. Air was then bubbled through the sample for approximately 5 minutes to raise the initial DO concentration. A magnetic stir bar was added to the sample bottle. The lid, fitted with a DO probe, was secured allowing the wastewater to overflow in order to insure zero headspace within the bottle. The sample was stirred using a magnetic stirrer and the DO concentration was recorded with time.

In the second method for measuring the oxygen uptake rate (the BOD-type experiment), 250 mL of sample was added to a pint amber glass respirometry bottle. The respirometry bottle lid has a tube fitting to allow the bottle to be connected to a mercury manometer. A T-connector was inserted in the manometer tubing; lithium hydroxide was poured in the side tube to absorb produced carbon dioxide and the side tube was sealed. The bottle was then clamped in a wrist-action shaker and sufficiently agitated to ensure that oxygen transfer was not rate limiting. The pressure drop resulting from aerobic (oxygen consuming) biological activity was measured with the mercury manometer as a function of time.

The initial oxygen consumption rate in the wastewater from Site A was 2.4 ± 0.2 mg/L-hr (95%) and 137 mg/L BOD was consumed after 90 hours. The data are summarized in Table 1.

The data from the oxygen depletion from Site B are presented graphically in Figure 2. A least squares linear regression was performed on the data and the calculated slopes provide the observed zero order oxygen utilization rates. Note that the data for the refinery wastewater sample do not fit a linear curve very well ($R^2 = 0.9813$).

Presuming that the reaction is first order in substrate concentration (i.e., BOD), the reaction rate equation becomes:

$$\text{rate} = -\frac{d(\text{DO})}{dt} = k(\text{BOD}). \qquad (1)$$

Since the DO uptake ($\text{DO}_{\text{up},t}$) is simply the difference in the original BOD (BOD_0) and the BOD at time t, Equation 1 can be rewritten as:

$$\ln(1 - \text{DO}_{\text{up},t}/\text{BOD}_0) = -kt. \qquad (2)$$

The BOD_0 value which best fit Equation 2 (i.e., y-intercept of zero) was 8.89 mg/L; the value of k at this BOD_0 was 0.0185 ± 0.011 hrs^{-1} ($R^2 = 0.9949$). Equation 2 yields a calculated BOD_5 value of 7.9 mg/L for the refinery wastewater sample. This is commensurate with the expected effluent BOD_5 values of 2.4 to 7.7 mg/L since some reduction in BOD will occur between the sampling point and the effluent.

The DO uptake rate for the lube oil wastewater sample remained fairly constant even though the absolute DO concentration fell below one. For the range evaluated, both the zero-order and the first order in BOD rate models were acceptable models in describing the rate of oxygen consumption. For the BOD rate model, the best BOD_o value was 18.53 mg/L, and the calculated first order rate constant was k = 0.0111 ± 0.0005 $hours^{-1}$ ($R^2 = 0.9969$). The BOD_5 of the lube oil wastewater sample calculated using the above equation is 13.6 mg/L. Again, this is commensurate with the expected effluent BOD_5 values of 8 to 12 mg/L since some reduction in BOD will occur between the sampling point and the effluent. Since the BOD rate model is the best model for both sets of data as seen by the correlation coefficients, the low concentrations of substrates are thought to be responsible for the slow oxygen uptake rates observed.

Some of the results of the oxygen uptake experiments for the Lagoon B samples at Site C are shown in Figure 3. A linear regression analysis was performed on the data and the calculated slopes provide the observed oxygen utilization rates. The DO uptake of the poisoned Lagoon B samples were minimal; when a BOD-type experimental sample was poisoned, oxygen consumption ceased. The oxygen uptake rates observed in the DO depletion experiments were slower than those observed in the longer term BOD-type experiments. Also, there was a noticeable lag phase in the BOD-type experimental oxygen utilization curves. These results are predictable in light of the _in situ_ DO measurements. The quick oxygen uptake rate observed experimentally and the low DO concentrations measured _in situ_ suggest that the bacteria present in the pond could utilize oxygen faster than it was provided. Consequently, the low DO concentration in the collected sample required much of the bacteria to acclimate to the oxygen-rich conditions of the experiments causing the lag phase and slow initial oxygen utilization rates. Apparently, the potential for aerobic biological activity was significant in Lagoon B, but its _in situ_ importance was limited by the slow aeration rate.

The long-term average oxygen uptake rates of the Lagoon B samples are very similar. The total amount of oxygen consumed by the different samples was also nearly identical. The total observed BOD of the Lagoon B wastewater was 2,050 mg/L; however, oxygen was still being consumed when the experiment was terminated.

The results of the oxygen uptake experiments for the Lagoon C wastewater sample were similar to those for Lagoon B. Specifically, these results were: the poisoned sample showed minimal oxygen utilization; the DO depletion experiment revealed a slower initial oxygen utilization rate than was observed with the longer BOD-type study; and there was a noticeable lag phase in the BOD-type experimental oxygen utilization curve.

The experimental results of Lagoon D wastewater suggested that chemical oxidation, not biooxidation, was the most significant oxygen utilization mechanism. The oxygen depletion rate of the poisoned and non-poisoned samples were identical.

The high pH of Lagoon E wastewater is prohibitive to biological growth. As this pond is upstream of Lagoon D, chemical oxidation is again believed to be responsible for its low _in situ_ DO concentration.

For each bulk wastewater sample at Site C, 700 mL of wastewater was placed in a 1-L amber glass bottles with teflon-lined screw caps. Identical samples with 700 mg of mercuric acetate was also examined. The 1-L bottles were continuously agitated and vented twice daily by blowing air into the headspace for 30 seconds. Relative component concentrations were determined by GC using headspace injections. Analytical samples were collected on Day 1, Day 3, and Day 8 of the study. (3)

The wind was flowing toward the east at approximately 200 ft/min (8 mph) during the sample collection at Site C. The sample taken from the west end of Lagoon B was near the impoundment inlet and was somewhat lower in concentration than the southeast corner sample initially.

Three major VO peaks were observed by GC headspace analyses. There was no significant trend of the first peak (34 sec.) area changes during the eight days of the test for the sample taken from the west end of the lagoon, but there were average increases of 20 percent per day for the first peak area from the sample taken from the southeast corner. These increases were only observed in one sample and could be due to experimental error.

For the second peak (55 sec.) there was no effect of biocide on the rate of change of the peak area. The sample taken from the southeast corner of the lagoon did not demonstrate a significant reduction in the 55 sec. peak area. The 55 sec. peak of the sample from the west end of the impoundment, however, declined 6 percent per day for both the sample of wastewater with biocide and without the biocide.

For the sample taken from the west end of the lagoon, the third peak (60 sec.) increased in area at roughly the same rate as the rate of decrease of the second peak (in the same sample). For the sample of wastewater taken from the southeast corner, there was no significant change in concentration, with biocide or without biocide, for either the second or third peaks.

Thus, no clear trends were observed for the aerobic destruction of any of the three major VO components in the headspace of the Lagoon B wastewater samples. The average percent change of total headspace VO (total peak area) over the eight day period with biocide present was zero, with a standard deviation of approximately 10 percent of the concentration. The average change for the total headspace VO without biocide was 18.3 percent, with a standard deviation of approximately 10 percent. These results suggest the possibility of a small change in VO due to biological activity over an eight day period that is somewhat greater than the experimental error. Lagoon B would be expected to have lower in situ aerobic rates than measured in the laboratory, since it was primarily anaerobic at the time of the sample collection.

For a typical mass transfer rate for volatilization of $2 \cdot 10^{-5}$ g mol/cm^2-sec, the time constant for a two meter deep impoundment is approximately 6 days (63% volatilization loss). This predicted volatilization rate is significantly greater than the aerobic VO removal rates measured in the Lagoon B samples (the samples with the highest biological oxygen consumption rates). Lagoon B at Site C did not have an aerobic zone more than a few centimeters, additionally suggesting that aerobic biodegradation does not compete well with volatilization for VO removal in at typical surface impoundments.

Anaerobic Biological Activity Testing

When the in situ DO measurements indicated the presence of an anaerobic zone (DO $<$ 0.5 mg/L), a wastewater sample was withdrawn from the bottom of the lagoon and tested for anaerobic biological activity as follows. Nitrogen was first bubbled through the five gallon sample to purge any oxygen from the system that may have been introduced at the time of sample collection. The lid, modified to accommodate a small tube, was secured, and the tube was run to a water filled inverted graduated cylinder. Gas produced by the system was thus collected by water displacement, and the volume of gas produced was measured.

Figure 4 shows the cumulative volume of gas produced by the anaerobic system from Site A. During the first month, only 35 mL of gas was collected. After this lag phase, the system exhibited an exponential growth phase as gas was produced quickly. The growth phase was followed by a saturated or steady state phase in which gas production (assumed to be related to metabolic activity) proceeded at a constant rate. In single population systems, the saturated phase is typically followed by a decline phase caused by substrate limitation. However, in this system, another exponential growth phase followed the saturated phase. This is believed to be caused by the old population shifting to a new substrate or a new population exhibiting growth on the decaying matter of the old population.

Since no anaerobic zones were found at Site B with the in situ DO measurements, no anaerobic biological activity tests were performed.

Although the wastewater impoundments at Site C are oxygen deficient, there was little anaerobic gas generation in the four wastewater samples tested from Lagoons B, C, and D. Some carbon dioxide absorption was possible due to the high pH. The rates are reported in Table 1.

Samples were withdrawn from the Site C anaerobic test samples periodically for chemical analysis. These samples were collected in duplicate in 40 mL VOA vials and killed at the time of collection by the addition of 1 mL of a 40 mg/mL mercuric acetate solution. Analytical samples were collected at t=0, Day 8, Day 14, and Day 55 of the study; these samples were refrigerated until analyzed. One set of samples was analyzed by GC using headspace injections (3). The duplicate set of samples was analyzed by GC using purge and trap (3). The results of the headspace analyses on lagoon samples in the anaerobic study show a dramatic increase in total area counts for each lagoon sample after 55 days. Sample D contained more compounds and in greater quantities than the other samples.

The limited anaerobic biological activity of Site C wastewater samples does not demonstrate removal of volatile organics from the lagoon; however, in the wastewater sample from the west end of Lagoon B, a VO peak which corresponded to toluene and one other VO peak showed major reductions with time. There was a large increase in a VO peak which corresponded to methanol with time.

CONCLUSIONS

1. A sampling and analysis method is presented to evaluate the rate of biological activity in surface impoundments. The measured rates of biological and chemical VO removal can be compared to predicted air removal rates to determine the relative importance of competing VO removal pathways.

2. Surface impoundment wastewater samples from all three wastewater treatment facilities demonstrated biological activity. Microorganisms were observable and oxygen utilization was measurable in each lagoon wastewater.

3. The rate of oxygen consumption varied greatly from site to site, ranging from 0.1 to 35 mg/L-hr. An unusually high rate of oxygen consumption, 38 to 48 mg/L-hr, in one lagoon was attributed to chemical processes rather than biological processes.

4. Compound specific headspace of aerated samples from Site C indicated a half-life of approximately 8 days for one of the compounds. Other compounds either did not change in concentration or exhibited an increase in concentration. Thus, the measured biological oxidation rates are less than the expected volatilization rates of VO from surface impoundments.

5. The rate of anaerobic gas generation was slow in the lagoons which were anaerobic in the field. Several weeks were required before the anaerobic gas generation began. The compound specific analysis of VO indicated either no change in VO concentration or an increase in VO concentration due to anaerobic processes. Two VO peaks showed major reductions in one wastewater sample. These results suggest that anaerobic processes are not a significant pathway for VO removal in impoundments.

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TABLE 1. MEASURED BIOLOGICAL RATES

Sample	Aerobic oxygen uptake rates (mg/L-hr)[a] DO depletion	BOD-type	Anaerobic gas generation (mL/L-hr)
Site A	2.4 ± 0.2	1.57 ± 0.10	0.022[b]
Site B			
refinery	0.079 ± 0.009	NA	NA
lube oil	0.171 ± 0.014	NA	NA
Site C			
Lagoon B, west	7.19 ± 0.37	34.9 ± 1.0	$9 \cdot 10^{-5}$
Lagoon B, SE	12.1 ± 0.45	33.8 ± 0.6	$2.3 \cdot 10^{-3}$
Lagoon C	2.85 ± 0.07	5.75 ± 0.34	$2.6 \cdot 10^{-3}$
Lagoon D	38[c] ± 5	47.8[c] ± 1.1	$1.2 \cdot 10^{-3}$

[a] Oxygen uptake rates were determined by using a least squares linear regression on the data; the 95% confidence interval is also reported.

[b] Initial rate was lower.

[c] Not biological uptake, see text.

FIGURE 1. DISSOLVED OXYGEN PROFILES

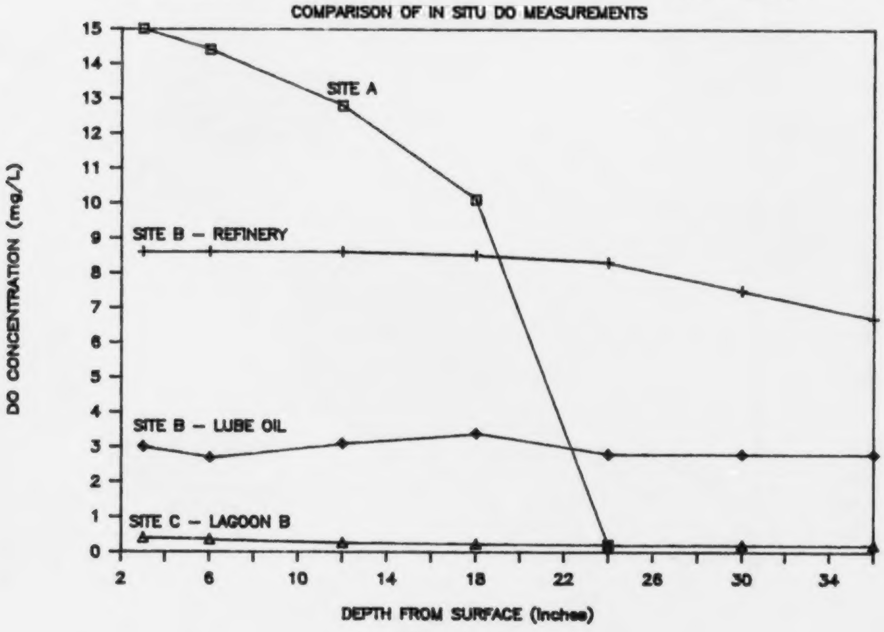


FIGURE 2. DO UPTAKE CURVE

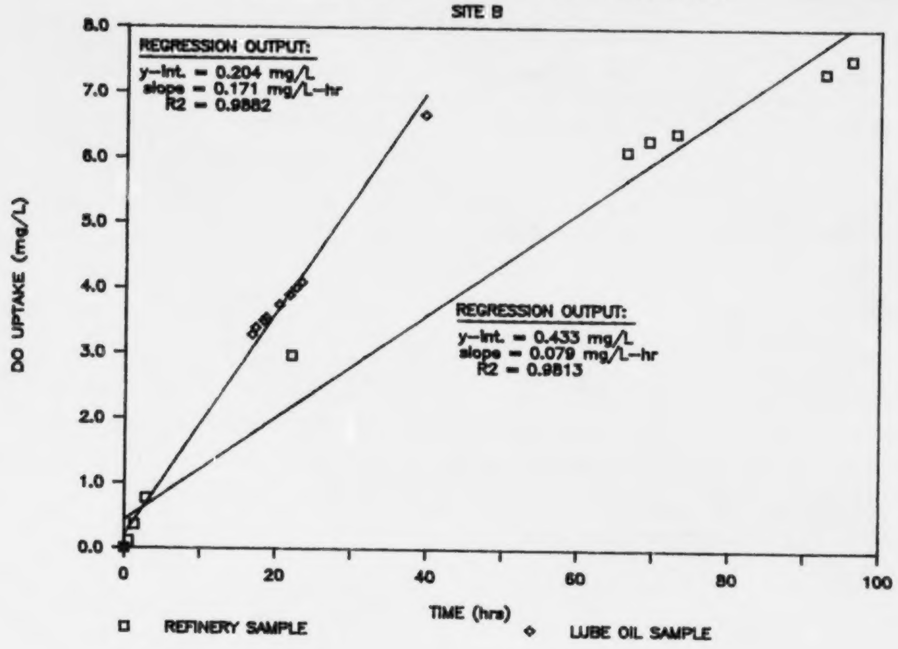


FIGURE 3. DO UPTAKE CURVE

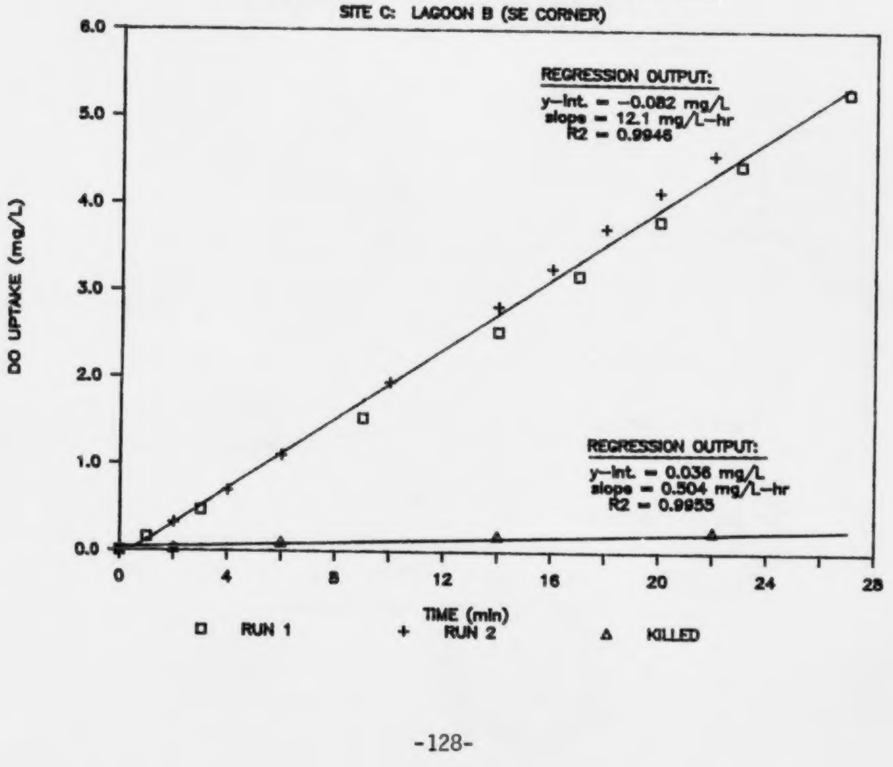
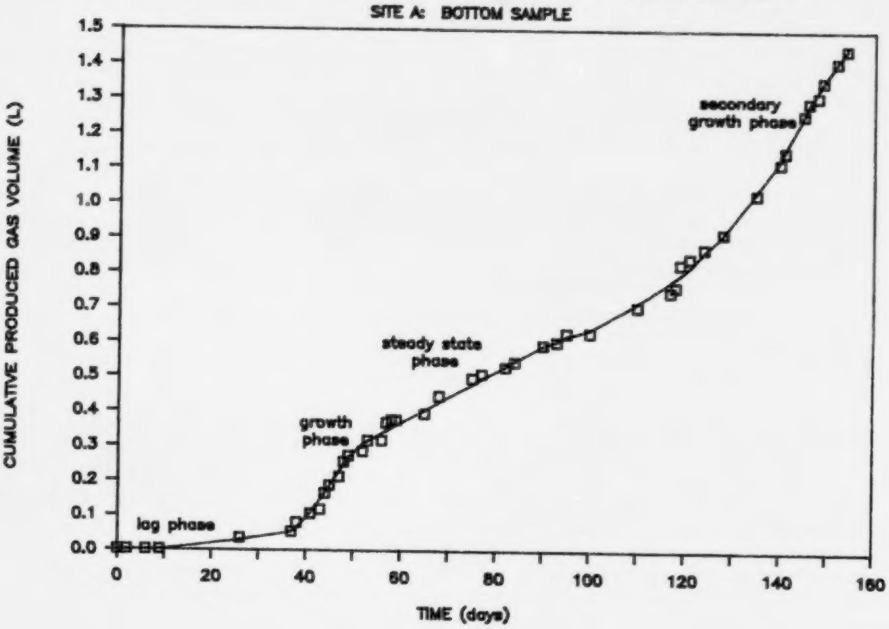


FIGURE 4. ANAEROBIC GAS PRODUCTION



COMPOSITION OF LEACHATES FROM ACTUAL HAZARDOUS WASTE SITES*

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ABSTRACT

This presentation addresses the analytical methodology used in a follow-on effort of a U.S. Environmental Protection Agency sponsored project. The project was initially undertaken to gather data on the composition of hazardous waste leachates and to support the development of multi-component synthetic leachate. These synthetic leachates will be used to evaluate the effectiveness of various liner materials used in landfills and other hazardous waste storage, treatment, and disposal facilities. As such, the formulated leachates should be representative of typical compositions of actual hazardous waste site leachates. During the initial study, the routine organic analyses of thirteen leachates accounted for only approximately four percent of the overall Total Organic Carbon (TOC). As a result, a more rigorous and complex analytical method was developed and is presently being employed in the follow-on study to obtain a more comprehensive characterization. During the first phase of this study, a hazardous waste leachate sample was characterized by the new analytical procedure with the intent of maximizing the percent of TOC accountable by specific compounds or by functional groups. Overall, approximately 48% of the TOC was accounted for by the new method. This included approximately 20% attributed to individual components and 28% accounted for by functional groups. In order to obtain more information on the actual composition of hazardous waste leachate, a second phase of this study is employing the same new analytical method to characterize two additional leachate samples. Based on the results of these more thorough characterizations, recommendations will be made regarding the composition of representative synthetic leachates for linear compatibility testing.

INTRODUCTION

A data base containing information on hazardous wastes and their associated leachate compositions is being developed by the Hazardous Waste Engineering Research Laboratory (HWERL) of the U.S. EPA Land Pollution Control Division. The data base will be used to develop a multi-component, synthetic hazardous waste leachate. The formulated leachate will be used to test the integrity of containment liners under consideration for use in landfills and other hazardous waste storage, treatment, and disposal facilities.

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In a previous study (1), thirteen hazardous waste disposal site leachates were analyzed for priority pollutant metals, organic compounds, total cyanide, total organic carbon, chemical oxygen demand, and a variety of other general parameters. The authors completely characterized the leachates for metal concentrations; however, the overall sum of identified organic constituents averaged to only about four percent of the sample TOC. Because liner compatibility tests have shown that heavy metals in saturated solutions are generally compatible with flexible membrane liners, the focus of this follow- on study has been to more thoroughly characterize the unidentified portion of the TOC.

Therefore, in order to maximize the accountable organic carbon, the first phase of this study was devoted to the development of a more rigorous analytical procedure, which would identify organic contribution by functional group classes or by individual compounds when possible. The method was evaluated by using it to characterize a leachate sample, and the results presented here indicate that the procedure is capable of a more complete organic characterization of hazardous waste site leachates. Additional insight into the actual organic composition of waste site leachates is the objective of the second phase of study, which will also allow for minor modifications to the method through the analysis of two different leachate samples. This paper describes the analytical methodology, results of the first phase analysis, recommendations for modifications to the procedure, and suggestions for areas of further study.

METHODS AND MATERIALS

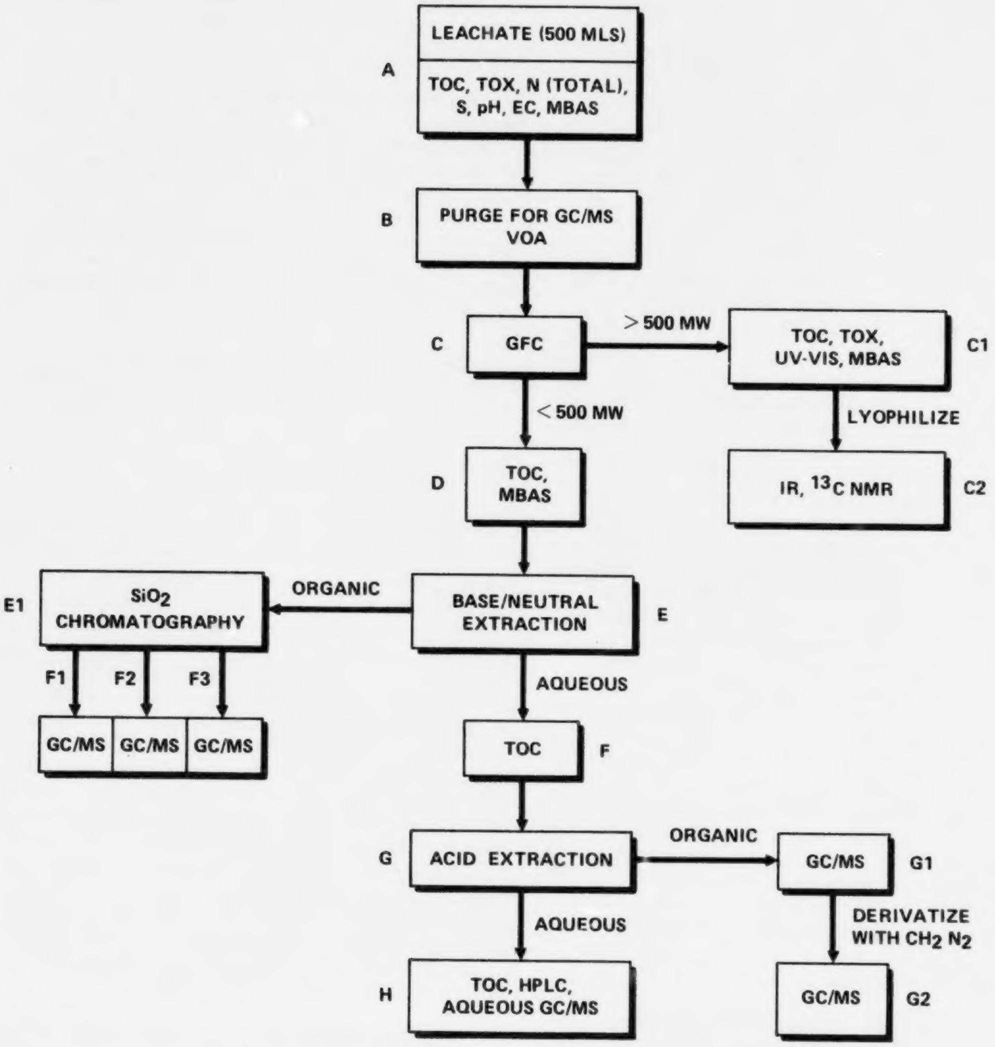
The analytical scheme that was developed is outlined in Figure 1. The procedure was designed to not only characterize organic priority pollutants, but also to identify polar compounds not usually analyzed in standard procedures. In addition, the method allowed for the characterization of higher molecular weight compounds through the identification of functional groups. Total organic carbon (TOC) measurements were made at various critical steps in order to track the organic carbon mass which thereby allowed for an assignment of the TOC by functional group.

As seen in the figure, initial characterization included total organic halides (TOX), total nitrogen, sulfate, sulfide, pH, conductivity, and methylene blue active substances (MBAS) as well as TOC. In addition to the more routine analyses, MBAS analysis allowed for an estimation of the percent TOC due to anionic surfactants or detergents which may not be chromatographable.

The next step (B) identified and quantified individual volatile compounds through gas chromatography/mass spectroscopy (GC/MS) purge and trap techniques. The purged sample was then subjected to a molecular weight fractionation using gel filtration chromatography (GFC). The >500 molecular weight (MW) fraction was analyzed for TOC, TOX, and MBAS for mass balance of those parameters and by UV-visible, and infrared spectroscopy and ^{13}C-NMR for functional group characterizations. After TOC and MBAS analysis, the <500 MW was extracted (neutral and basic) followed by silica gel chromatography of the extract into aliphatic, aromatic, and polar fractions with subsequent GC/MS analysis. The aqueous remainder was re-analyzed for TOC, then extracted after acidification. After GC/MS analysis the extract was subjected to derivitization with diazomethane followed by reanalysis in order to verify compound identities. The aqueous remainder after acidic extraction was analyzed by high pressure liquid chromatography (HPLC) and aqueous compatible capillary column GC/MS and, finally, TOC.

A brief description of each step shown in Figure 1 follows. The figure also lists the QA/QC measures taken at each of the steps including replicates, field blanks, spike and recovery, and method blanks.

Step A Raw leachate was obtained from a hazardous waste site in New Jersey and submitted to SAIC with a field blank of distilled water. The collection of the


LEACHATE (500 MLS)
TOC, TOX, N (TOTAL), S, pH, EC, MBAS
A
PURGE FOR GC/MS VOA
B
GFC
C
> 500 MW
TOC, TOX, UV-VIS, MBAS
C1
LYOPHILIZE
IR, 13C NMR
C2
< 500 MW
TOC, MBAS
D
BASE/NEUTRAL EXTRACTION
E
ORGANIC
SiO2 CHROMATOGRAPHY
E1
F1
F2
F3
GC/MS
GC/MS
GC/MS
AQUEOUS
TOC
F
ACID EXTRACTION
G
ORGANIC
GC/MS
G1
DERIVATIZE WITH CH2 N2
GC/MS
G2
AQUEOUS
TOC, HPLC, AQUEOUS GC/MS
H

QA ANALYSES:

REPLICATES AT STEPS A, B, C1, D
FIELD/METHOD BLANKS AT A, B, C1, D, E1, E2, F, G2, H
SPIKED BLANKS AT STEPS E, E1, E2, G, G1

Figure 1. Diagram of phase II analytical steps.

field blank consisted of opening the appropriate sample container (filled with distilled water) for the duration of the leachate sampling. Aliquots of the leachate and field blank were taken for TOC, TOX, total nitrogen, sulfate, MBAS, sulfide, pH and conductivity (EC).

TOC measurements were made using an O.I. Corporation Model 700 TOC analyzer, and followed the US EPA 600/4-79-020 Method 160.4(4). TOX was measured on a Xertex/Dohrmann DX-20 analyzer, following the US EPA Method 9020. All the other analyses were done following procedures outlined in Standard Methods for the Examination of Water and Wastewater (5) and the particular methods for each analyte are as follows: nitrogen by method 420A; sulfate by method 426D; MBAS by method 512B; sulfide by method 427; EC by method 205; and pH by method 423, using an Altex 4500 pH meter with an Orion 8104 probe.

Step B A 5 ml aliquot of the raw leachate was analyzed by GC/MS for volatile organic compound characterization according to EPA Test Method 624.

The remaining leachate was purged with Ultra pure nitrogen for 24 hours at a rate of approximately 100 mls N_2/minute. An aliquot was analyzed by GC/MS to assure total removal of volatile organic compounds. A 500 ml aliquot of the purged leachate was used in Step C.

Step C The molecular weight fractionation step presented here was completed using gel filtration chromatography techniques. In order to calibrate the GFC separations, one column (20 mm x 300 mm with a 250 ml reservoir) was static-packed to the 300 mm mark with Sephadex® G-10-120, which has an average pore exclusion size of 700 daltons. The water exclusion volume was calculated (3) to be 31 ml and, after a 10 ml application of the leachate, this quantity was collected and discarded. Next, 10 ml fractions were eluted and collected for three bed volumes. Three additional bed volumes were taken in 15 ml fractions, for a total of fifteen fractions. These fractions were extracted and analyzed by GC/MS for determination of molecular weight.

The results obtained were plotted as molecular weight versus volume eluted in mls. The relation was linear, and indicated that all compounds of molecular weight greater than 500 were eluted in the first 34 ml (very close to the calculated volume). All compounds were eluted in 142 ml.

Steps C1, C2, & D Aliquots of the MW >500 fraction were analyzed for TOC and TOX, in duplicate, with accompanying field blanks. Aliquots of the <500 MW fraction were analyzed for TOC only. The analytical scheme calls for MBAS analysis of Steps C1 and D; however, because no MBAS were detected during Step A, further MBAS analyses were eliminated.

The >500 MW fraction was also scanned on a Hitachi 100-80 UV/VIS spectrophotometer (with recorder) from 800 nm to 190 nm. The scan was conducted with the field blank in the reference cell using matching quartz cuvettes.

Lyophilization of this fraction (to remove water) was accomplished by placing approximately 75 mls of sample at a time in a 500 ml round bottom flask fitted with a ground glass adapter. Vacuum tubing connected the flask and adapter to a trap which was placed in a dewar containing liquid nitrogen. A vacuum was applied to the system using a Welch Duo-Seal® vacuum pump. Ice was removed from the trap periodically and discarded. The complete contents of the fraction were lyophilized in this fashion and the resulting solid was quantitatively recovered.

Upon completion of the lyophilization, a small quantity of the solid was pressed into a potassium bromide (KBr) pellet, and subjected to infrared spectrophotometry using a Perkin-Elmer Fourier Transform Infrared Spectrophotometer connected to a Perkin-Elmer 7300 Series computer. Scans were from 4000 cm^{-1} to 600 cm^{-1} and referenced against air. The solid was also subjected to ^{13}C NMR, using a GE 300 series model. The sample was dissolved in D_2O, spiked with dioxane (as an internal standard) and run at a 45 degree pulse to allow for relaxation.

Steps E, E1, E2 and G The <500 MW fraction was spiked with Base/Neutral/Acid surrogate standards to a final concentration of 200 ng/μl. The fraction was then extracted with methylene chloride at pH 7, pH 12 and pH 1. A small aliquot was taken for TOC analysis before acid extraction (Step F). The base and neutral extracts of the spiked leachate were combined. The combined extract was volume reduced in a concentrator tube to ~1 ml then exchanged into hexane. The reduced extract was then subjected to silica gel chromatography, using a column of 10 mm i.d. x 240 mm with a 200 ml reservoir. Three fractions were collected (aliphatic, aromatic, and polar) corresponding to elution by 1) 50 mls of pentane, 2) 200 mls of 1:1 pentane; methylene chloride and 3) 50 mls of methylene chloride. Each fraction's volume was reduced and then analyzed by GC/MS.

Steps G1 and G2 The acid extract was also volume reduced and screened by GC/MS for compound identification and quantification. After initial screening and compound identification, the extract was derivatized with diazomethane.

This derivitization converts carboxylic acids to esters and alcohols to ethers. Diazomethane for the reaction was produced according to the method of H.M. Fales, T.M. Jaouni and J.F. Babashak (2). This method is of considerably lower hazard than most conventional methods, while producing CH_2N_2 in good yield. Once derivatized the sample extract was reanalyzed by GC/MS for compound-specific identification confirmation.

Step H After acid extraction the aqueous remainder was aliquoted for TOC, HPLC and aqueous GC/MS techniques. Aqueous GC/MS analysis was conducted using a J&W Scientific Carbowax Fused Silica capillary column. HPLC was done using a Waters Associates Model 244 LC with a R401 Refractive Index Detector. This particular model does not run gradients in the mobile phase; therefore, runs were done with 100% methanol; 75% methanol and 25% H_2O; 50% methanol and 50% H_2O; 25% methanol and 75% H_2O; and 100% H_2O. All runs utilized a C-18 reverse phase column.

RESULTS AND DISCUSSIONS

The analytical approach described above was applied to a waste site leachate sample with the initial (Step A) characteristics shown in Table 1. As seen, this sample has elevated TOC and conductivity and a depressed pH, moderate to high levels of nitrogen, sulfate and TOX, and undetected levels of sulfide and MBAS.

GC/MS purge and trap analysis for volatile organic constituents identified 18 compounds mostly present in the low part-per-billion (ppb) range. The most abundant volatile compounds were toluene at 143 ppb and vinyl acetate at 114 ppb. The remaining compounds included ketone solvents, chlorinated solvents, aromatic and aliphatic hydrocarbons and alcohols in the low (<50) ppb range. The total level of volatile organic carbon (374 μg/l) represents <0.01% of the initial sample TOC.

Table 1. INITIAL LEACHATE CHARACTERIZATION (STEP A)

Analyte	Units	Field Blank	Sample Average
Nitrogen (total)	mg/l	<10	635
Sulfate	mg/l	<3	210
Sulfide	mg/l	<10	<10
MBAS	mg/l	<0.1	<0.1
pH		6.9	4.3
Conductivity	umhos/cm	10	19,500
TOC	mg/l	<3	16,000
TOX	mg Cl/l	0.07	166

Figure 2 tracks the TOC distribution by weight percent according to the analytical steps employed. As seen, the molecular weight fractionation step by gel filtration chromatography resulted in the loss of 29% of the TOC due to adsorption or reactions with the Sephadex® gel. The remaining TOC was almost evenly distributed between the less than and greater than 500 molecular weight fractions. Based on ^{13}C-NMR and proton NMR, the 39% TOC observed in the greater than 500 MW fraction was determined to be comprised primarily of aromatic hydrocarbons. This data was in good agreement with fourier transfer infra-red (FTIR)

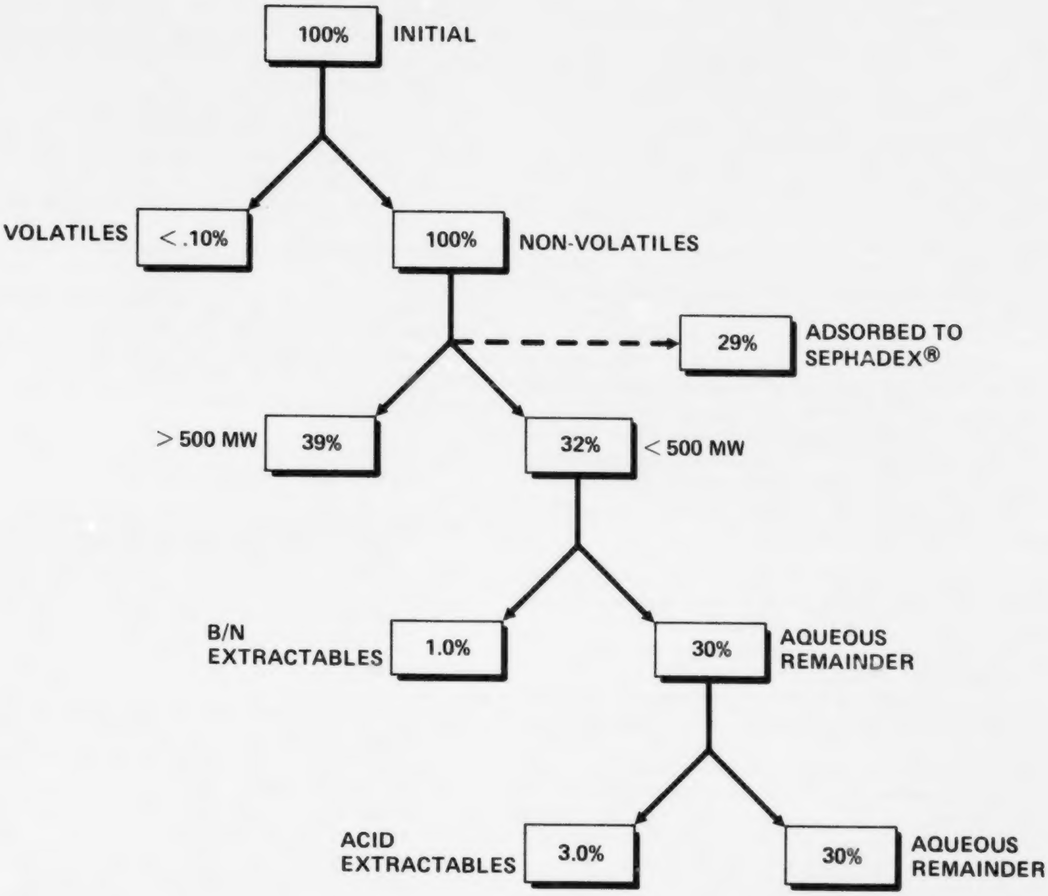

100%
INITIAL
VOLATILES
< .10%
100%
NON-VOLATILES
29%
ADSORBED TO SEPHADEX®
> 500 MW
39%
32%
< 500 MW
B/N EXTRACTABLES
1.0%
30%
AQUEOUS REMAINDER
ACID EXTRACTABLES
3.0%
30%
AQUEOUS REMAINDER

Figure 2. TOC distribution flow scheme by percentage.

spectroscopic analysis which showed only an OH absorbance and aromatic overtone resonances. In addition, this higher molecular weight fraction contained nearly 20% of the original TOX.

The results of base/neutral extraction of the <500 MW fraction with subsequent silica gel chromatography indicate that the aliphatic fraction (F1) consisted solely of low level n-alkane concentrations. The aromatic fraction (F2) had only three compounds present, two of which were not identifiable by GC/MS. The highest levels of base/neutral extractable carbon were present in the polar fraction (F3) with phenol exhibiting the highest concentrations. The total contribution to the TOC resulting from base/neutral extractable compound level is approximately 1.0%.

Another 3.0% of the initial TOC was accounted for during acid extraction. The largest contribution is due to benzoic acid and phenol, with pentanoic and hexanoic acids also present in substantial concentrations. Subsequent diaxomethane derivitization was used primarily for compound identification confirmation.

The remaining aqueous phase after both GFC and base/neutral and acid extraction was found to retain 30 percent of the original TOC. The composition of this "remainder" fraction was determined by aqueous GC/MS, and was found to be composed primarily of benzoic acid with some phenol as well. The benzoic acid concentration was exceedingly high in this fraction, and this individual compound alone accounts for 17% of the entire initial TOC value. Table 2 shows the other major individual compounds contributing to the TOC. As seen, over 20% of the leachate TOC can be attributed to benzoic acid and phenol.

TABLE 2. TOC CLASSIFICATION BY MAJOR INDIVIDUAL COMPOUNDS

Compounds	% of Original TOC
Benzoic Acid	17.
Phenol	3.1
Pentanoic Acid	.07
Hexanoic Acid	.06
Trimethyl-1,3-pentanediol	.08

Table 3 presents the leachate composition as a function of organic functionality, with representative compounds and their contribution. These six general organic functional classes are often used to assess the compatibility of organic compounds with various contaminant liners. The largest contribution was from aromatic hydrocarbons of molecular weights greater than 500. The only other class of compounds to contribute substantially to the TOC was organic acids, with benzoic acid responsible for the vast majority of the TOC. All the other classes were responsible for less than 1% of the overall TOC, with organic bases not contributing at all.

CONCLUSIONS AND RECOMMENDATIONS

The results of the waste site leachate characterization by the analytical procedure developed and utilized during this study provide the basis for the following conclusions:

- The method accounted for approximately 48% of the organic carbon present.
- The major constituents are organic acids (20%) and aromatic hydrocarbons (26%). The organic acid group consists primarily of benzoic acid. The aromatic hydrocarbon contribution is attributed to high (>500) molecular weight aromatic compounds.
- The procedure allows for a more thorough characterization of the sample by providing steps to ensure the recovery of highly water soluble, polar compounds. Standard separatory funnel solvent extraction methods were capable of recovering only a small fraction (13%) of the total mass of benzoic acid present. Therefore the procedure calls for aqueous GC/MS, and HPLC steps, which were used successfully to quantify the organic acid contribution.
- Reactions with and/or adsorption to the Sephadex® gel during GFC resulted in the loss of 29% of the sample TOC.

Based on the conclusions above, recommendations for further studies would include 1) the optimization of the molecular weight separation step and 2) a more detailed investigation into the composition of the >500 molecular weight fraction.

TABLE 3. ORGANIC CONTENT BY CHEMICAL CLASSIFICATION

Chemical Classification	Percent (WT)	Representative Compounds
Organic Acids	20.3	Benzoic Acid (17.1%) Phenol (3.1%) Alkanoic Acids (0.13%) Substituted Benzoic Acids (0.01%) Substituted Phenols (0.002%)
Oxygenated Hydrocarbons	0.08	Ketone Solvents (0.0003%) Alcohols (0.0002%) Trimethylpentanediol (0.08%)
Halogenated Hydrocarbons	0.86	TOX (0.86%) Chlorinated Solvents (0.001%)
Organic Bases	0.0	None detected
Aromatic Hydrocarbons	26.8	Aromatic Compounds >500 MW (26.8%) Benzene and Alkyl-substituted benzenes (0.001%)
Aliphatic Hydrocarbons	0.002	n-alkanes (0.002%)

Because the molecular weight separation step was directly responsible for the loss of 29% of the TOC, this procedure should be modified to affect a clean separation while minimizing the loss of organic carbon. In addition to testing other available gel chromatography materials, efforts should be directed towards resources (such as fractional vacuum distillation) that might circumvent organic carbon losses. With that additional organic carbon available for characterization, accountable TOC may exceed 80% (based on the loss experienced using Sephadex® gel for molecular weight separation).

The molecular weight separation step is important because it can effectively isolate a large portion of the organic carbon that normally would not be accounted for. Of the six chemical classifications, the >500 molecular weight fraction of aromatic hydrocarbons exhibited the highest percentage of organic carbon (26.8%). Because this fraction represents a substantial portion of the overall organic carbon and because synthetic leachate formulations should include representative constituents from this fraction, additional studies should focus on the specific chemical composition of the >500 MW fraction.

Once a more efficient molecular weight separation step has been devised we recommend that a statistically sufficient number of representative leachate samples be subjected to the procedure. A comprehensive data base, containing the fully characterized organic portion of actual waste site leachates, will greatly facilitate the formulation of a synthetic leachate. This approach, in combination with the newly developed analytical method, will ensure that containment liner compatibility tests are conducted with a realistic and accurate representation of actual waste site leachates.

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DECONTAMINATION TECHNIQUES FOR MOBILE RESPONSE EQUIPMENT USED AT WASTE SITES

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ABSTRACT

Any cleanup equipment used at waste sites must be decontaminated after use. This paper highlights a published EPA report on the state-of-the-art review of decontamination techniques for cleanup equipment and discusses field experience with decontaminating equipment presently in use.

For those who prepare decontamination plans for cleanup equipment at hazardous sites, the EPA report provides background material on decontamination methods, contamination assessment, and contamination avoidance. The EPA report particularly stresses the importance of contamination avoidance. Such measures as use of enclosures for equipment, safety features on equipment to prevent spills and leaks, and protective coatings on equipment surfaces reduce hazard, time, and cost of the final decontamination task.

Though chemical methods are being developed to degrade contaminants on equipment surfaces, use of physical removal methods prevails in the field. This will be shown in discussing decontamination procedures of equipment presently in use, such as the EPA Mobile Incineration System operating at the Denney Farm Site, Missouri, on dioxin-contaminated oils, sludges, and soils.

INTRODUCTION

Any equipment used at a waste site must be decontaminated prior to its removal from the site. This paper highlights a published EPA state-of-the-art review entitled "Decontamination Techniques for Mobile Response Equipment Used at Waste Sites," and discusses field practices with decontaminating equipment presently in use at dioxin-contaminated sites in EPA Region VII. Personnel protective clothing and equipment and decontamination of personnel is not a subject of this paper, though mention of it is made where appropriate. Decontamination is a separate field activity with full-time personnel assigned to it. Like any other field operation at a site, decontamination must be planned for, executed in the field, and tested for its effectiveness. A decontamination plan constitutes a separate section of any operating permit or any other workplan pertaining to the site activities. The decontamination plan for the EPA Mobile Incineration System operating at the Denney Farm Site in Missouri is an example of such a plan.

The EPA report is particularly useful to those who are new to the responsibility for equipment decontamination, either in the planning stage or in the field. For example, the report should be useful to those who develop and design new treatment systems for use at waste sites and to those who introduce existing systems to process hazardous waste. The report gives background material on decontamination methods, contamination assessment, and contamination avoidance.

Decontamination methods for large and expensive components of mobile response equipment should be non-destructive to the equipment itself, but effective in removing contaminants from interior and exterior surfaces of the equipment. Small items may be sacrificed and/or disposed of. Determination of an acceptable level of contamination is essential. Development and testing of decontamination methods may be necessary prior to taking equipment to the field. Contamination assessment ment is done with chemical and physical test(s) that are able to test down to the determined acceptable level of contaminants on equipment. Some test methods may need to be developed.

The report stresses the importance of contamination avoidance because, if appropriate measures are taken, both the decontamination and the contamination assessment can be much reduced and simplified.

Field decontamination practices presented here are those of EPA Region VII. EPA Region VII has gained considerable experience with decontamination of various equipment used at many dioxin-contaminated sites in Missouri. Decontamination has been performed at all levels of site activities such as field investigation, excavation and removal of contaminated materials, and ultimate disposal and delisting of residues with the use of the EPA Mobile Incineration System at the Denney Farm Site, Missouri. Region VII practices contamination avoidance. The amount of equipment that would require decontamination is kept to a minimum. They accomplish it by using disposable equipment and by wrapping reusable equipment with disposable coverings. For equipment that cannot be protected, Region VII has developed a rigorous decontamination procedure. Equipment decontamininated with this procedure is then wipe-sampled and released only when analysis of wipe samples show non-detectable levels of dioxin.

IMPORTANCE OF CONTAMINATION AVOIDANCE

Contamination avoidance is an important consideration of any planned or ongoing activity at a waste site because it reduces hazard, time, and cost of the final decontamination task. The report discusses such measures as use of enclosed structures and secondary containment for the mobile response units, equipment safety features, and protective coatings for mobile response equipment. Region VII has developed a number of practical ways to minimize contamination in all of their activities at dioxin-contaminated sites. Contamination avoidance has been carefully considered for the EPA incinerator at Denney Farm.

Enclosures for Equipment

A combined use of an overhead structure with a secondary containment is an effective measure to minimize transport of hazardous materials during operation of the mobile response equipment and to facilitate the decontamination task. An example would be a "Butler" steel building attached to a concrete slab.

Housing of equipment by an overhead structure is not always required, but it minimizes air transport of contaminants during its operation. A variety of commercial temporary or semi-permanent structures are available at a cost of $30-$400 per square meter as shown in Table 1.

Table 1. Overhead Temporary Structures

Structure Type	Cost Per Square Meter
Air Inflatable	$ 30 - $100
Steel Arch	$100 - $200
Fabric Supported by Arch	$200 - $400
Prefabricated Steel ("Butler")	$ 80 - $100

Secondary containment to catch spills, leaks, or wash solution from the decontamination operation is always required. It can be applied either under the entire operating unit or at points of the unit where leaks or spills are most likely. A simple and effective secondary containment can be a sloped, combed concrete slab, coated with a polymeric material and with a collection sump. It can also provide structural support for the operating system. Another simple and commonly used secondary containment is a polymeric fabric cover, such as polyurethane or polyethylene.

Safety Features

Safety features on equipment to prevent spills and leaks is another means to prevent contamination of equipment surfaces. Most important here is the design of the equipment itself to have few potential sources of fugitive emissions. The next step is to examine system components, identify those that may break during operation, and either change or reinforce them. Failures typically occur in seals and fittings used in such components as pumps, valves, and piping systems. See Table 2.

Table 2. Equipment Components Using Seals and Fittings

Component	Point of Potential Failure	Comment
Pumps	Drive shaft seals	Use sealless pumps
In-line Valve Open-ended Valve	Stem and bonnet Stem, bonnet, and flow seal	Use bellows-sealed valves and diaphragm valves
Piping System	Flanges, elbows, and tees	Minimize sharp elbows. Use high-temperature/high-pressure seals. Use stainless steel or Inconel pipes.

Protective Coatings

Protective coatings of paint or polymeric materials, either permanent or temporary, can provide a barrier between equipment surfaces and contaminants. For mobile equipment, those that are promising are temporary coatings that can be peeled off and disposed of by incineration, for example. For small areas protective tapes can be used. Protective coatings on response equipment, except for tapes, are not used at waste sites. See Table 3.

Table 3. Protective Coatings for External Equipment Surfaces

Coatings	Quantity of Waste Produced	Cost	Danger to Operator	Comment
Permanent (Epoxy resins)	Moderate	Moderate	Low	Not suitable for mobile equipment
Temporary (Polyvinyl Chloride)	Moderate to Large	Moderate to Large	Low to Moderate	Two or More Coatings Needed

Contamination Avoidance at Region VII

Region VII's approach to contamination avoidance on dioxin-sites is to use disposable equipment and wrapping equipment with disposable coverings. Among disposable equipment is most of the personnel protective gear and equipment such as Tyvek® suits, spent cartridges from respirators, occasionally boot covers, and inner and outer gloves. These items are discarded whenever they are removed at lunch breaks or at the end of the day.

Other disposable equipment are sampling spoons, sample trays, and survey flags. Disposing of small sampling equipment reduces chances for cross-contamination of samples, which is another benefit. Disposable plastic covers are used to protect surfaces of reusable items. The exterior of sample jars is kept free of contamination with this method. Prior to sample collection, the jar is placed into a plastic bag with the opening sealed around the top of the jar with a rubber band. After filling the jar with the sample, the bag is pulled off and discarded. Disposable coverings are also used to protect large containers, so called roll-off boxes, for transporting bulk excavated soil from other sites to the site where the incinerator operates. The boxes are first triple lined with polyethylene sheeting. After filling with soil, the sheeting is sealed and boxes are topped for transport. At the feed storage building, the back of the boxes are opened, the boxes are tipped, and the plastic wrapped soil package slides out of the box into the storage building. The interior and exterior of the roll-off boxes remains free from contamination and does not require decontaminating. Also, the exterior of the wrapped soil package is free from contamination. Of course, discarded items and coverings add to the bulk of hazardous waste. Availability of the incinerator as at the Denney Farm makes it possible to dispose of this waste by incineration. The contamination avoidance for the EPA incinerator at Denney Farm is achieved by situating main components of the system in the clean zone. Only the material storage building for loose soil and the building housing the shredder and waste oil tank are situated in the contaminated zone. A completely enclosed conveyor brings the shredded feed to the completely enclosed loading area of the incinerator, which is located in the clean zone. The incinerator is also housed in a building, though the primary reason for constructing this building was weather protection of the system and comfort of operating personnel.

Pre-cleaning of Equipment Before and After Travel

Another helpful technique to prevent buildup of contaminants on equipment surfaces is to clean the equipment prior to its transport from the home base to the site and upon arrival at the waste site. The entire incineration system was steam-cleaned within three days before leaving its home base in Edison, New Jersey, to remove oil and dirt, and this operation was repeated upon arrival at Denney Farm to remove accumulated road dirt.

DECONTAMINATION PROCEDURES

Decontamination procedure by a single method or a sequence of methods removes or detoxifies the residual contaminants from the internal and external surfaces of the equipment. The decontamination procedure has to be designed for the particular hazardous substance(s) to be treated, and also tested on equipment prior to its use in the field. Any decontamination is usually time consuming and labor intensive. Region VII designed and tested a decontamination sequence for the dioxin-contaminated equipment.

The report divides decontamination procedures into three categories: solubilization methods, which use solvents to solubilize and wash off contaminants, chemical degradation methods which chemically degrade contaminants at the surface, and mechanical methods, which mechanically detach contaminants from the surface with abrasive and non-abrasive methods.

Solubilization Methods

For the mobile field equipment, solubilization methods are primarily used because they are available, effective, non-destructive, and suitable for both internal and external surfaces. These methods use water or steam, with or without detergents, organic solvents, and foams, gels, and pastes. Use of foams, gels, and pastes may give better coverage of equipment surfaces than a thin organic solvent. Application of wash solutions is usually by immersion or spray. The disadvantage of these methods is that they generate waste, usually liquid, that contains the removed contaminant. See Table 4.

Table 4. Decontamination of Surfaces by Solubilization Methods

Method	Quantity of Waste Produced	Cost	Danger to Operator	Comment
Water	Large	Low	Low	Detergents and/or surfactants increase effectiveness.
Steam	Small	Moderate	Moderate	Detergents and/or surfactants increase effectiveness. Can spread contaminants.
Organic Solvents	Moderate	Moderate to High	Moderate	May be toxic or flammable.
Foams	Small	Moderate to High	Low	
Gels and Pastes	Small	Moderate to High	Moderate	Not for internal surfaces.

Chemical Degradation Methods

Chemical degradation of surface contaminants can be a one-step treatment, and generated waste, if any, could contain no contaminant. These methods are mainly in the developmental stage. Methods presented in Table 5 are commercially available. Flash lamp cleaning with pulse ultraviolet radiation that delivers localized, short-lasting, very high temperatures is a promising emerging method for destruction of surface contaminants. The removal mechanism depends on the contaminant and treatment conditions. The contaminant can be photochemically reduced, vaporized, incinerated, pyrolyzed, or, in the presence of water, "steam cleaned." Some such lamps are used for specialized cleaning operations. Lamps can be operated safely.

Table 5. Decontamination of Surfaces by Chemical Degradation Methods

Method	Quantity of Waste Produced	Cost	Danger to Operator	Comment
High Intensity Light (Xenon Lamp)	Small	Low to Moderate	Low	Most effective on flat surfaces. For external surfaces only.
UV Light Cleaning	Small	Low to Moderate	Low	Most effective on flat surfaces. For external surfaces only. Developmental stage.
Electropolishing of Metal Surfaces	Moderate	Moderate to High	Moderate	For small parts that can be immersed. External and internal surfaces.

Electropolishing systems can be used on a variety of alloy systems if parts can be disasembled and immersed in the liquid bath. After treatment, the metal must be rinsed off, dried, and painted.

Mechanical Methods

Mechanical decontamination methods can be abrasive or non-abrasive to the equipment surfaces. Abrasive methods are destructive to the equipment and generate large amounts of waste.

Table 6. Decontamination of Surfaces by Abrasive Methods

Method	Quantity of Waste Produced	Cost	Danger to Operator	Comment
Pigs	Moderate	Low	Low	For internal surfaces like pipes
Brushes	Moderate	Low	Moderate	
Wet Abrasives	Large	Moderate	Moderate	Destructive to equipment
Dry Abrasives	Large	Moderate	High	Destructive to equipment
Dry Ice Blasting	Small	Moderate	Moderate	

Table 7. Decontamination of Surfaces by Non-Abrasive Methods

Method	Quantity of Waste Produced	Cost	Danger to Operator	Comment
High-Pressure Water (200-700 atm)	Moderate to Large	Moderate	Moderate	For loosely adhering contaminants.
Ultra-high Pressure Water (1000-4000 atm)	Moderate to Large	Moderate to High	Moderate	For tightly adhering contaminants.
High-Pressure Freon 113™	Small	High	Low	Cleans cloth, rubber, and plastic.
Ultrasonic	Small	Low to Moderate	Low	Effective for cleaning small parts that can be immersed.
Vacuum with Filters	Small	Low	Low	For loosely adhering contaminants.

Of mechanical methods presented in Table 6 and Table 7 in field use are vacuum systems with a HEPA filter or an activated carbon filter, brushes, ultra high-pressure water at 1,000 atm, and high-pressure Freon 113™. All these systems are commercially available.

Decontamination of Equipment at Region VII

The EPA Region VII decontamination procedure for dioxin-contaminated equipment consists of a five step sequence. This procedure is:

- Tap water and detergent (Alconox) wash/scrub (1 part "Alconox" and 3 parts water);
- Tap water rinse;
- Deionized water rinse;
- Methanol or Isopropyl alcohol rinse;
- Air dry.

The above procedure was developed early in the Missouri dioxin investigations and was tested with quality assurance/quality control (QA/QC) of wipe and rinsate samples prior to its present routine use. The procedure is used on all field equipment such as backhoes, forklifts, front-end loaders, drill rigs, trucks, and trailers. The cleaned equipment is wipe-sampled and released only when the analysis shows acceptable levels of dioxin, not higher than 100 ng/m^2. This procedure will be used on some components of the EPA incineration system before it leaves the Denney Farm site. The procedure is labor intensive, particularly for large equipment. It takes three people a day or more to decontaminate a large piece of equipment.

The operators performing decontamination wear protective clothing and equipment that is required by the level of hazard in the operating zone; usually it is Level C of personnel protection.

Decontamination equipment in use at Region VII consists of the following: steam jenny; vacuum with a HEPA filter; tanks or containers for clean solutions such as tap water, deionized water, and alcohol; garden hoses and spray nozzles; brushes and rags; and wipe test sampling sets and jars for liquid or solid samples. If possible, spent wash solutions are discarded into the ground in the contaminated zone; some of it is used to moisten the feed going to the shredder; sometimes alcohol is allowed to evaporate.

However, at the end of the cleanup operation, and after the incinerator leaves, the remaining wash solutions must be treated.

Most decontamination operations at dioxin sites in Region VII are performed in the open. The location of the operation is always at the border between contaminated and clean zones so that decontaminated equipment is moved into the clean zone. However, use of an enclosed structure with catchments for fumes, wash solutions, or solid waste, may be desirable when many items of equipment are to be decontaminated with a variety of methods.

Also, some enclosed decontamination systems for equipment are commercially available.

CONTAMINATION ASSESSMENT OR TESTING

The need for decontamination and effectiveness of decontamination are determined by analyzing samples taken from interior and exterior surfaces of the equipment, and samples of wash solutions or other wastes generated by the decontamination operation are also analyzed. The starting point is to determine the acceptable level of decontamination of equipment surfaces. This enables the selection of both suitable decontamination and analytical procedures. In the case of dioxins, the decontamination level is the same as the detection level, which is the the worst case.

Sampling and analytical procedures for decontamination assessment and the number and location of samples to be taken are specified in the decontamination plan.

Most convenient for analysis of surface contaminants in the field would be an instant instrumental reading. The report describes a portable fluorometric monitor for polynuclear aromatic hydrocarbons on a variety of surfaces, such as metals, plastics, and fabrics. The monitor was in the developmental stage at the time the report was written.

For analysis of dioxins, wipe samples are taken from surfaces and sent to the laboratory. In Region VII, wipe samples are analyzed within 24 hours so the decontaminated equipment can be released the next day.

SUMMARY

Decontamination of mobile response equipment operating at a hazardous waste site is a requirement. Any measure taken to prevent contamination will reduce hazard, time, and cost of the future decontamination operation.

Both decontamination and contamination assessment procedures should be selected and tested before taking equipment to the field. In some cases, development of either decontamination procedure or testing procedure, or both, may be necessary or desirable.

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LEAK PREVENTION IN UNDERGROUND STORAGE TANKS:

A STATE-OF-THE-ART SURVEY

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ABSTRACT

The objectives of this state-of-the-art survey were to examine the design and operational practices associated with underground storage tank (UST) systems and to identify areas for further research and development that would advance leak prevention technology.

Many standards, guidelines, and recommended practices for the design and operation of UST systems are currently promulgated by several professional and industrial organizations. However, many of these procedures have overlapping requirements and there is no way of confirming how widely they are understood or followed in the field. Consequently, there is a need for a cohesive and coordinated set of rules and standards that apply to various types of UST systems, including those that store chemicals, and for further work to assess and improve operating practices, including spill prevention and leak detection methods and devices.

BACKGROUND

Protecting the nation's groundwater resources from contamination by regulated substances* that leak† from underground storage tank (UST) systems has emerged as a major environmental issue. More than 50 percent of the nation's population draw drinking water from underground sources. There are between 2 and 3.5 million underground tanks buried across the nation, of which some 100,000 tanks are estimated to be presently leaking, and some 350,000 are expected to leak within the next 5 years. Accordingly, the need to improve leak prevention technology is evident.

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*Regulated substances are those substances defined in Section 101 (14) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, and petroleum, including crude oil or any fraction thereof which is liquid at 60°F, and 14.7 pounds per square inch absolute pressure.

†In this paper, the word "leak" denotes all unauthorized releases.

FACTORS AFFECTING LEAK PREVENTION

Preventing leaks in UST systems requires consideration of several factors, including the system characteristics (e.g., age, ownership, product stored, size, etc.) and the elements of the solution scheme (e.g., design and engineering, fabrication and installation, operation, corrective actions, etc.).

System Characteristics

The age of an UST system influences the solution option. Leak prevention technology is designed and engineered into new systems. In old installations, it is a reactive step requiring system monitoring, retrofitting, remediation and restoration. Identifying the problem is the significant step in an abandoned installation.

UST system ownership affects leak prevention. Large industrial owners have the technical, managerial, and financial resources and the economic and legal impetus to employ effective prevention strategies. Small owners lack money and organization to develop their own methods and procedures to prevent and remediate leaks. They require training in understanding the dimensions of the problem, reliable methods and procedures for solution, and incentives that compel them to apply leak prevention programs.

The largest class of regulated substances stored in UST systems is gasoline and other petroleum products. Accordingly, these have been the primary focus of leak prevention investigations thus far. The problem, however, extends far beyond this. The list of regulated substances includes 698 chemicals which are stored in USTs. The different physical and chemical properties, toxicity, transport, and fate characteristics of such regulated substances require different approaches to leak prevention.

The size of USTs has a significant influence on leak prevention strategy. Leak rates from large installations are likely to be higher than from smaller installations. Size differences also present problems as regards to construction materials, design, inspection procedures, leak monitoring, repair, maintenance, and replacement schedules.

Elements of the Solution Scheme

A leak prevention strategy should ensure the integrity of the containment boundaries for the life of the system; avoid or minimize accidental spills and overflows; provide warning of impending leaks; and prevent the spread of leaking products. These tasks require: proper design, engineering, fabrication and installation, correct operation, and appropriate corrective actions through inspection, repair, and maintenance. These requirements can be satisfied by applying valid principles of mechanics and other engineering sciences; ensuring quality of materials and workmanship; providing appropriate tools and equipment; establishing appropriate schedules for inspection, repair and maintenance; and enforcing appropriate standards and regulations.

DESCRIPTION OF UNDERGROUND STORAGE TANK SYSTEMS

A basic UST system includes tanks, piping, and accessories.

Tanks

Eighty-nine percent of existing USTs are carbon steel. Carbon steel is compatible with petroleum products, inexpensive, available, easy to fabricate and repair, strong, and relatively resistant to damage. However, most carbon steel USTs are not protected against corrosion.

Tanks that have corrosion protection include steel tanks with internal and external coatings; cathodically protected steel tanks; fiberglass-reinforced plastic (FRP) tanks, and steel-FRP-bonded composite tanks.

FRP tanks are a composite consisting of a plastic resin matrix with a fiberglass reinforcement. The resins must be compatible with stored product(s) and the surrounding environment. An estimated 24 percent of USTs storing petroleum products use FRP tanks. Steel-FRP-bonded tanks have a steel inner shell and an FRP outer layer fused by a polyester resin bond. These combine the strength and stiffness of steel with the corrosion resistance of FRP. Tanks made of stainless steel, aluminum, and various plastics are used in limited applications.

Piping

Pipes used in USTs are made of a variety of materials, including: carbon steel; cast iron; stainless steel; galvanized steel; rubber, plastic, or epoxy-lined steel; plastic; and fiberglass-reinforced plastic. The same considerations that enter into the selection of the tank material apply to the piping selection. For example, carbon steel pipes are compatible with petroleum; however, they are susceptible to corrosion when they are kept in contact with corrosive chemicals. On the other hand, cast iron pipes resist corrosion well and can be used to carry concentrated acids. They are brittle, however, and can break on impact or shock. Both carbon steel and cast iron are relatively inexpensive.

Accessories

Accessories in an UST system include valves, pumps, joints, fittings, vapor recovery systems, overfill prevention systems, and leak monitoring ports.

Secondary Containment

Secondary containment retains leaks from a basic UST system, aids their detection, and facilitates their cleanup. Secondary containment can be accomplished in two ways: (1) by building a barrier between the basic system and the surrounding ground with flexible membrane liners, a concrete vault, clay liners, or soil sealants; or (2) by using a double-wall structural configuration for tanks and pipes. Both methods can be used in combination.

DESIGN AND ENGINEERING PRACTICES

Properties of Products

Physical, chemical, and hazard characteristics of stored products are important UST design considerations. Critical characteristics include the product's physical state at ambient temperature, melting point, boiling point, specific gravity, vapor pressure, explosivity, flammability, combustibility and corrosivity.

When products stored in an UST system comprise a mixture, the consequences of combining the constituent chemicals must also be evaluated. One method for determining these consequences is a chemical class compatibility matrix (1). The method is based on grouping chemicals into 38 classes based on similar molecular structure and similar reactivity characteristics. Possible consequences (e.g., heat generation, explosion, violent polymerization, etc.) of mixing one class of chemicals with another can be indicated for ready design reference.

Mechanical Forces

Mechanical forces imposed on an UST system and its components include: dead loads due to product weight, self weight, weight of soil overlay, reaction forces, etc; live loads due to internal pressure, thermal expansion forces, vehicular traffic; and environmental loads due to wind, buoyancy pressure due to groundwater table, seismic load in earthquake-prone zones. While most current designs are based on manufacturer specifications and industry standards, there are sophisticated design methods and analytical tools available to determine optimal configurations, dimensions and layouts of UST systems.

Corrosion

Corrosion is a major cause of deterioration and failure of metallic UST systems. It can occur internally and externally. Internal corrosion is largely due to the incompatibility of the stored product with materials of construction. External corrosion is usually influenced by soil resistivity; moisture content; type and concentration of salts in the soil; presence of certain types of bacteria; temperature; permeability of surface film; presence of adjacent underground metallic structures; and stray underground electrical current.

Corrosion can be prevented by providing cathodic protection that forces an electric current toward, rather than away from, UST components, or by selecting materials of construction that inhibit electric flow altogether. Two design concepts used for cathodic protection include sacrificial anodes and impressed-current systems.

Materials of Construction

Materials used in UST systems include various types of metals and polymeric materials. Structural strength and compatibility with products and soil environment are two key factors that determine the choice of materials. The American Society for Testing Materials (ASTM) has the most universally accepted standards for construction materials. However, these standards do not include exposure to all hazardous chemicals listed as regulated substances. Consequently, UST manufacturer guidelines and specifications should be consulted for selection of appropriate materials.

Codes and Standards

For the purpose of design classificaton, UST systems may be grouped into: systems that operate essentially at atmospheric pressure; low-pressure systems that operate at pressures up to 15 psig; or high-pressure systems that operate at pressures higher than 15 psig.

Many technical standards, guidelines, and recommended practices generated by professional, trade, and industrial organizations exist for the design of these systems. Most of the documents that apply to atmospheric systems are developed by the American Petroleum Institute, American Water Works Association, and Underwriters Laboratories. Most standards and design guidelines that apply to lower-pressure systems are from the American Petroleum Institute and the American Society of Mechanical Engineers. The ASME Boiler and Pressure Vessel Code, by adoption, is a legally binding standard in most states and local jurisdictions for design, construction, and operation of high-pressure systems. The American Petroleum Institute and the National Fire Protection Association also have some codes pertinent to high-pressure systems.

Several states have already established, or are in the process of establishing, UST regulations incorporating many of the previously mentioned guidelines. These include California, Connecticut, Florida, Maine, Maryland, New Jersey, New Hampshire, New York, and Rhode Island.

INSTALLATION TECHNIQUES

Improper installation of UST systems is a common cause of leakage. Proper installation and testing procedures that are based on sound engineering principles can reduce such leakages. These procedures include: investigation of soil conditions and characteristics; selection of materials of construction appropriate for design conditions; selection of proper bedding and backfill material; handling and care of equipment during construction; tightness testing requirements; and supervision requirements.

Although state regulations vary, most of them require the installation of double-walled tanks or secondary containment systems such as flexible membrane liners, concrete vaults, clay liners, and soil sealants; overfill protection; leak monitoring wells; and leakage alarm systems. Each system has very specific guidelines pertaining to installation procedures, cost differentials, and environmental conditions.

Piping and Accessories Installation

Selection, installation, and testing of UST system piping must be based upon appropriate standards and guidelines. Field connections must be made properly and protected against corrosion. This involves the cleaning and preparation of the surfaces to be connected, proper use of thermowelding or mechanical clamps, and application of effective corrosion protection to the bare areas before backfilling.

OPERATING PROCEDURES AND GUIDELINES

Professional, trade, and industrial organizations have developed operating procedures and guidelines concerning overfill prevention, transfer spill prevention, vapor recovery, and leak detection and monitoring. There procedures are designed to prevent the release of products during filling and transfer operations, and to enable prompt recognition of underground leaks that result from impairment of tanks, pipes, or accessories.

Overfill Prevention

An ideal overfill prevention system includes a level-sensing device equipped with an alarm to alert the operator of an impending overfill and an automatic product shutoff when the tank is full. Many states have specific regulations pertaining to overfill protection. These range from automated overfill systems to delivery operator determination to manhole containment.

Transfer Spill Prevention

Proper operating practices that should be followed to prevent transfer spills are well documented. These practices require: tight connections between the hose and fill pipe; periodic inspection of all transfer hoses; inspection of tank ullage before product delivery to ensure sufficient capacity; proper identification of stored products and container capacities; and proper training of all operators who perform loading or unloading operations.

Vapor Recovery Systems

Gasoline vapors and volatile organic compound emissions from UST systems may violate ambient air quality standards. These releases occur during UST filling and vehicle refueling. Vapors are also emitted from truck tanks as gasoline displaces the gasoline-enriched air in the tank. These vapors can be controlled by venting through charcoal filters in the truck tank itself or back into the UST.

Leak Detection

Leak detection is an integral part of the regulatory requirements associated with preventing leaks. Several states already have such requirements. Methods and strategies for leak detection include: inventory control, continuous in-tank leak monitoring, nonvolumetric methods, leak effects monitoring, and tank integrity testing.

Inspection

Proper inspection of tanks and other UST components is carried out before, during, and after the system is installed and operated to determine the structural integrity of the system and to evaluate possible corrective actions should problems be found. Inspection of existing UST systems is difficult, if not impossible, unless provisions have been made for inspection ports, manways, and other means of access.

A quality inspection program should identify excessive corrosion, erosion of interior parts due to abrasion by particles suspended in moving fluids, structural fatigue or cracking, deterioration of liners and accessories, and weakened or cracked welds and joints. Formal checklists, records of inspection, and frequent inspections ensure a quality program.

Physical, nondestructive inspections of UST systems are not always possible nor do they always give a reliable assessment of the UST system's integrity. Thus, predictive methods, based on theoretical or empirical models, supplement physical inspections and aid in scheduling tests, maintenance, and repair. Two predictive models proposed and used by the Petroleum Association for Conservation of the Canadian Environment (PACE) are the Soil Aggressiveness Value (SAV) method (2) and Roger's Regression Analysis (3).

The SAV method is based on the premise that the age at which an underground storage tank leaks is directly related to the surrounding soil condition. The soil condition is characterized by a SAV which is an aggregate number determined on the basis of the following soil properties: average values of soil resistivity, soil pH, and soil moisture; differential values (i.e., the ranges of resistivity and pH); and presence of sulfides (which promote bacterial action on the surface of the tank).

The data obtained by the PACE on tank age at failure, and the corresponding SAV, have been developed into a tank evaluation graph (Figure 1). The region below the curve S, given by the equation SAV x Age = 69, represents a 95 percent confidence bound for occurrence of no leaks. The higher the SAV x Age value, the higher the probability that the tank will leak. The curve SAV x Age = 180 envelopes 40 percent of all leaks. Based on these analyses, PACE recommended the following corrective actions:

Region	Recommended Action
1. $I \geq 180$	Replace tank
2. $69 \leq I < 180$	Test, and replace or retrofit
3. $I \leq 69$ and $SAV \geq 4$	Retrofit
4. $I < 69$ and $SAV \leq 4$	Benign, no corrective action warranted

where I = SAV x Age

Roger's regression analysis method is based on a statistical analysis of the age-to-leak data correlated to measureable characteristics of the tank environment. The correlation equation for mean age-to-leak is given by:

$$L = 5.75\ R^{.05}\ T^{-.107}\ \exp\ (.12^{P} - .42\ M - .26S)$$

where L is the mean-age-to-leak in years; R is the soil resistivity in ohm-cm; T is the tank size in Imperial gallons; P is the soil pH; M is a factor related to moisture content in the soil (1 for saturated, 0.5 for damp, and 0 for dry); and S is a factor related to sulfides content in the soil (1 for strongly present, 0.5 for trace, and 0 for no sulfides).

It is claimed that approximately 75 percent of the total variability in the dependent variable L is explained, with a high degree of statistical significance, by the full set of independent variables included in the model. Roger's equation, exercised with four sets of values for independent variables, results in a mean age-to-leak range from 13.5-16 years, with an average of 14.9 years. This prediction is close to variously reported mean ages-to-leak of 17-19 years.

It should be noted that this method does not allow for changes in the values of the independent variables that would, most likely, occur, e.g., in soil resistivity and moisture content, during the life of the tank system. Also, the method assumes that tank failure occurs as a consequence of only the external soil properties without any influence of internal condition.

MAINTENANCE AND REPAIR

There are presently no standard inspection, maintenance, or repair practices available for tank owners. However, many states are introducing regulations for such practices. This will require qualified inspectors, testers, and maintenance personnel trained to recognize impending failures, and to respond with appropriate corrective actions. Designers, manufacturers, installers, and suppliers must provide input to develop procedures and practices that can be easily implemented by the owners and operators of UST systems.

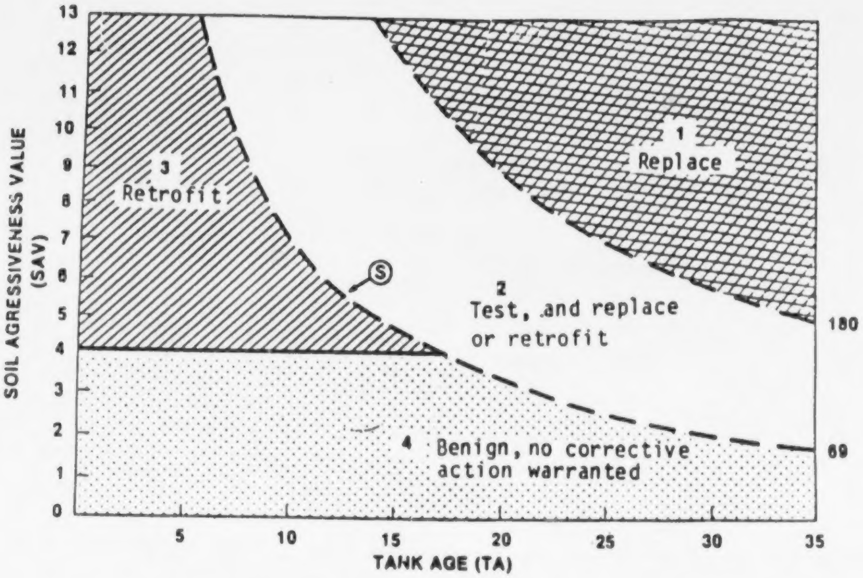

Figure 1. Tank evaluation graph

CONCLUSIONS AND RECOMMENDATIONS

Many standards, guidelines, and recommended practices for the design and operation of UST systems are currently promulgated by several professional and industrial organizations. However, many of these procedures have overlapping requirements and most of them apply only to systems that store gasoline products. There is need for a cohesive, coordinated set of rules and standards that apply to various classes of UST systems.

The available statistical information does not provide a correlation of failure rates and failure mechanisms with different design configurations, materials of construction, soil conditions, and environmental and operational factors. Additionally, the effects of long-term exposure of materials of construction of UST systems to different types of products and outside soil and backfill materials are not known. There is a need to develop these data and protocols for selection of materials applicable to specific conditions.

Various agencies and institutions provide installation procedures and guidelines. However, at present there is no way to determine how well these procedures and guidelines are understood and followed by installers. Efforts to improve operating practices should focus upon three areas: methods, equipment, and people. Adequacy of spill prevention methods, leak detection methods and devices, and operator training require special attention.

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A PRELIMINARY ANALYSIS OF UNDERGROUND TANKS USED FOR CERCLA CHEMICAL STORAGE

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ABSTRACT

The scope and severity of leaking underground storage tanks (USTs) containing chemicals have not been well defined. A study was undertaken for the United States Environmental Protection Agency (EPA) to collect and analyze data on USTs with the goals of (1) obtaining better information on the chemical UST population and (2) developing a strategy to rank underground tanks according to the hazard potential of their stored chemicals. The study addresed only Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) chemicals. Information sources included State surveys in California and New York and data from the Chemical Manufacturers Association (CMA). The analysis considered the nature (physical-chemical and toxicological properties) of the stored chemicals, tank population, size and age of tanks, materials of tank construction, and means of tank corrosion protection.

Solvents constitute the bulk (70-90%) of the organic CERCLA substances stored in USTs. As reported by CMA, the most prevalent organic solvents (acetone, methanol, toluene, methylene chloride, and xylene) constituted over 50% (both by number of tanks and volume stored) of all CERCLA substances in USTs. The average tank size reported by California and New York was 6,000 gallons, while those reported by the CMA was 15,000 gallons. The average tank age reported by CMA was 18 years. The majority are single walled, steel tanks that are protected against corrosion only by paint.

INTRODUCTION

The recent and rather sudden realization of the real and potential dangers to human life, environment, and the economy from leaking underground storage tanks (UST) has resulted in major regulatory efforts by federal, state, and local governments. On the federal level the Resource Conservation and Recovery Act (RCRA) was reauthorized and signed by the President in November of 1984. Subtitle I of this Act directs the United States Environmental Protection Agency (EPA) to promulgate regulations to control leakage from USTs. Deadlines mandated are: registration by owners of all tanks with the states by May 1986, estabishment of new standards for petroleum USTs by February 1987, and establishment of new standards for chemical USTs by August 1988. Some states have undertaken parallel action by promulgating their own regulations for UST control [1]. The major thrust of ongoing research is currently directed toward petroleum products, while relatively little attention is being paid to chemicals stored in underground tanks. This paper is based on a project that defined the physical universe of CERCLA chemical USTs. Included are the nature (physical-chemical and toxicological properties) and the quantity of stored chemicals, as well as the size, design, and construction characteristics of USTs. The objective is to provide a factual basis for the prioritization of UST leak control research (as a function of the stored chemicals).

The EPA divided UST leak control research into three main categories, i.e., leak detection/monitoring, leak prevention, and corrective action. As indicated, research has begun for petroleum tanks. The main emphasis is on volumetric leak detection methods (e.g., those based on changes in liquid level). State-of-the-art information has also been compiled for petroleum tank leak prevention and corrective action; however, chemical tanks have not yet been addressed. As a first cut, this project used a matricized ranking method for CERCLA chemical hazard potential to enable EPA to optimize a research program strategy for chemical tanks. Along with volume and number of tanks, the matrix included toxicity, ignitibility/reactivity, and viscosity/density of stored chemicals.

The results of this analysis will primarily be used for an intelligent estimate of the national hazard potential of stored chemicals. From this, chemicals can be grouped and prioritized for UST research and regulatory purposes. Chemicals with similar physical-chemical properties will be grouped together. The properties (including toxicity) will be used for hardware compatability requirements, industrial hygiene standards (human handling requirements), and signal-sensing requirements for volumetric (liquid level) leak detection. These groupings will further be used in developing a logical research progression in the prevention and corrective action categories, and will provide an important reference/database for on-scene decision-making in the case of corrective action needs.

SCOPE

Since EPA has mandated deadline for new standards for CERCLA chemical USTs, this project was designed to provide a logical foundation for chemical UST leakage control research. Aside from petroleum, Subtitle I of the reauthorized RCRA, defines regulated substances as those chemicals that are listed under Section 101 (14) of CERCLA [2], excluding hazardous waste.

All 611 CERCLA chemicals (excluding those substances that fall under the CERCLA categories of waste streams) defined by Section 101 (14) were considered in this study. Specifically, an attempt was made to determine:

a) composition of regulated substances stored underground
b) number and volume of tanks storing each substance
c) UST design characteristics, including materials of construction and corrosion protection
d) age of tanks.

SOURCES OF INFORMATION

Chemicals that require underground storage because of either flammability or other safety hazards are produced and handled by the commercial community that can be classified as:

- Primary Producers
- Formulators - Distributors
- Ultimate Users

The relative number of underground storage tanks increases from top to bottom in this classification scheme.

Commerce generally dictates the nature and quantity of chemicals developed by the primary producers. The primary producers provide large quantities of these chemicals in bulk storage for use by the chemical formulators who combine these chemicals into useful products and sell them to industrial, agricultural, and household users. Chemical distributors perform a similar function by repackaging. The great majority of tanks are owned by chemical users, such as manufacturing, agricultural, and service operations. Principal sources of UST information used in this study were State surveys in California [3,4] and New York [5]. Additional information was provided by CMA, a trade organization that represents primary chemical producers nationally [6].

REPRESENTATIVENESS AND COMPLETENESS OF DATA

Available state sources of UST information included: summary reports from California representing 100% of its UST users [3,4] and a computer data base file of hazardous substances stored in USTs in New York [5] representing approximately 90% of the New York UST population. A CMA survey of its members (178 companies representing 90% of primary chemical producers) [6] resulted in a 34% response of its membership. The product of this survey is a list of tank capacities, contents, status, (in use or abandoned), construction, corrosion protection, and age.

Each information source provided a different perspective on the universe of USTs. The CMA data are national in scope and, while somewhat incomplete, nevertheless indicate general patterns prevailing in the primary producing industry. California is a large southwestern coastal state with an integrated industrial/agricultural base and a significant contribution of new technologies. New York is a large northeastern state, with a broad industrial/agricultural base and a preponderance of the more traditional industries. Together these States represent about 20% of the estimated national UST population and all levels of commercial structure. Both new and traditional industries are well represented. Taken individually, the data sources are only fragments of the overall picture but, when examined together, they reveal the patterns prevailing on a national scale. This can be seen (Table 1) in the similarity of data for organic substances as reported by each source of information.

DISCUSSION

Reported data included:

1. Chemicals defined by an appropriate chemical name or Chemical Abstract Services (CAS) number. (Some chemicals fell under the definition of RCRA Subtitle I, but others did not.) CAS numbers are not cited in this paper.
2. Substances with generic or waste definitions, (e.g., mineral spirits, resin solutions, mixed solvents, slop water, polymers, and alcohols).

As previously discussed, this study is concerned only with specific chemical substances that are designated by the Subtitle I definition. Waste streams, mixtures, and impurities are not included.

Predominant Types of Chemicals Stored Underground

The CMA data shows that approximately 92% by volume of the CERCLA hazardous substances stored in USTs are organic in nature (inorganic compounds comprise the remainder). The data (Table 1) show that solvents are by far the largest single type of organics stored in USTs. Monomers rank next and the balance is comprised of miscellaneous substances. The percentages of organic compounds reported by CMA are similar to those reported in the California and New York state surveys. Table 2 provides more detail by listing the organic chemicals in each class.

Differences, however, were observed between inorganic substances reported in the three surveys. The data analysis suggests that the chemical users -- hardware manufacturing, electroplating, electronics, military, and aerospace -- make extensive use of USTs for storing acids, bases, heavy metal and salt solutions.

Percentage of UST Devoted to Storage of CERCLA Substances

The California survey shows that 166,973 USTs are registered [3]. The number of USTs that store CERCLA chemicals is 3,766 [4], or 2.25% of the registered total. The current number of UST registered in New York state is 78,819 and 792 (1.07%) are classified by the state as containing CERCLA chemicals [5]. Based on this information, it appears that the percentage of underground tanks devoted to storage of CERCLA chemicals is rather small and is probably in the 1 to 2 percent range of the total population (that includes petroleum product USTs) on a national basis.

UST Design Characteristics

The data (Table 3) indicates that the great majority of New York and CMA USTs that store chemicals are made of steel (94%) and are single walled. The remainder are made of concrete, copper, fiberglass, aluminum, or polymeric materials. More than one-half (56%) of the tanks are protected only by paint and only 18% have cathodic protection; the remainder use tar and fiberglass coatings. The age of USTs ranges between brand new and 60 years. The mean and median ages are each 18 years [6].

CONCLUSIONS

Both organic and inorganic substances are stored in underground tanks. The organics constitute the major part (92%) of CERCLA chemicals stored underground by major chemical producers. Significant amounts of inorganic substances, however, are stored underground by users of chemicals in hardware manufacturing and in electroplating. Seventy to 90% of the organic substances stored underground are solvents, including: alcohols; ketones; alicyclic, aromatic, and chlorinated hydrocarbons; esters; and ethers. Monomers and miscellaneous chemicals constitute the balance. Based on the California and New York data, it appears that only a small fraction (1 to 2 percent) of the total UST population is devoted to storing CERCLA chemicals. Petroleum products comprise 98-99% of the total liquids stored in USTs. The top five CERCLA chemicals stored underground are acetone, methanol, toluene, xylene, and methylene chloride. These five solvents represent over 50% of the CERCLA organics stored underground.

The majority of underground tanks used for storing chemicals are made of steel and are single walled. More than half are corrosion protected only by paint. The average tank size reported by the two states is 6,000 gallons, while CMA data show that primary chemical producers use tanks of a larger size (15,000 gallons).

The conclusions from this study are based on an organized and logical ranking of the stored substances and will aid the EPA in developing a research and rulemaking program for leak detection, prevention, and corrective action of CERCLA hazardous substances stored in USTs.

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TABLE 1
PREDOMINANT TYPES OF ORGANIC CHEMICALS STORED UNDERGROUND

(by percent*)

	California		New York		CMA	
	1	2	1	2	1	2
SOLVENTS						
Ketones/aldehydes	35.6	32.9	25.2	31.5	23.5	21.7
Aromatic hydrocarbons	22.2	21.1	37.8	32.9	21.8	22.3
Alcohols	10.2	8.8	16.5	17.2	18.8	16.8
Chlorinated hydrocarbons	12.5	14.0	5.7	4.0	12.6	10.3
Esters	6.0	4.4	6.2	4.4	1.2	0.8
Alicyclic hydrocarbons	0.6	0.7			0.4	0.4
Total solvents	87.1	81.9	91.4	90.0	78.3	72.3
MONOMERS	3.6	6.2	2.8	1.6	13.3	22.2
MISCELLANEOUS CHEMICALS	7.4	7.0	6.0	8.0	8.8	5.0
PESTICIDES	1.4	4.2				

Note: 1=number of USTs; 2=volume of USTs

* Totals may not sum to 100% because of rounding

TABLE 2
MAJOR ORGANIC CERCLA SUBSTANCES STORED IN USTs

Chemical Groups	California				New York				CMA			
	1	%	2	%	1	%	2	%	1	%	2	%
Ketones/Aldehydes												
Acetone	441	22.8	2334	18.0	43	12.0	319	18.3	98	17.8	1682	19.1
Methyl ethyl ketone	205	10.3	1254	9.6	32	9.0	122	7.0	21	3.8	145	1.6
Methyl isobutyl ketone	38	1.9	235	1.8	12	3.8	78	4.5	8	1.5	66	0.8
Cyclohexanone	7	0.4	45	0.4	--		--		1	0.2	2	<0.1
Formaldehyde	14	0.7	401	3.1	3	0.8	30	1.7	1	0.2	20	0.2
Acetaldehyde	2	0.1	10	0.1	--		--		--		--	
Total	707	35.6	4282	32.9	90	25.2	549	31.5	129	23.5	1915	21.7
Aromatic Hydrocarbons												
Toluene	265	13.3	1847	14.2	80	22.4	369	21.1	72	13.1	1481	16.9
Xylene	162	8.1	818	6.3	54	15.5	205	11.7	31	5.6	300	3.4
Benzene	9	0.5	28	0.2	1	0.3	1	0.1	10	1.8	120	1.4
Ethyl Benzene	5	0.3	47	0.4	--		--		7	1.3	56	0.6
TOTAL	441	22.3	2740	21.1	135	37.8	575	32.9	120	21.6	1957	22.3
Alcohols												
Methanol	131	6.6	714	5.5	41	11.5	149	8.5	87	15.8	1309	14.9
n-Butanol	46	2.3	277	2.1	14	3.9	146	8.4	11	2.0	130	1.5
iso-Butanol	25	1.3	158	1.2	4	1.1	5	0.3	4	1.0	37	0.4
TOTAL	202	10.2	1149	8.8	59	16.5	300	17.2	102	18.8	1476	16.8
Alicyclic Hydrocarbons												
Cyclohexane	12	0.6	67	0.7	--		--		2	0.4	63	0.4

Note: 1=number of USTs; 2=volume of USTs in thousands of gallons

TABLE 2 (cont.)
MAJOR ORGANIC CERCLA SUBSTANCES STORED IN USTs

Chemical Groups	California				New York				CMA			
	1	%	2	%	1	%	2	%	1	%	2	%
Chlorinated Hydrocarbons												
Methylene chloride	56	2.8	269	2.1	5	1.4	13	0.7	47	8.5	666	7.6
Methyl chloride	6	0.3	21	0.2	1	0.3	4	0.2	10	1.8	31	0.4
1,1,1-Trichloroethane	71	3.6	250	1.9	9	2.5	12	0.7	6	1.1	99	1.1
Trichloroethylene	18	0.9	71	0.5	2	0.6	11	0.6	2	0.4	80	0.9
Dichloropropane	1	<0.1	10	0.1	--		--		3	0.4	24	0.3
Chlorobenzene	3	0.2	3	<0.1	1	0.3	30	1.7	1	0.2	3	<0.1
1,2-Dichloropropane	--		--		--		--		1	0.2	4	<0.1
Chloroform	12	0.6	465	3.6	--		--		--		--	
Ethylene dichloride	13	0.7	367	2.8	1	0.3	1	<0.1	--		--	
Tetrachloroethylene	36	1.8	146	1.1	--		--		--		--	
Pentachlorophenol	12	0.6	144	1.1	--		--		--		--	
Carbon tetrachloride	3	0.2	28	0.2	1	0.3	1	0.1	--		--	
Trichlorobenzene	3	0.2	11	0.1	--		--		--		--	
1,2 Dichloro ethylene	1	<0.1	10	0.1	--		--		--		--	
Methyl bromide	1	<0.1	10	0.1	--		--		--		--	
Ethylene dibromide	1	<0.1	9	0.1	--		--		--		--	
1,1,2-Trichloroethane	3	0.2	3	<0.1	--		--		--		--	
TOTALS	247	12.5	1823	14.0	20	5.7	71	4.0	69	12.6	907	10.3
Esthers												
Ethyl acetate	22	1.1	111	0.9	7	2.0	23	1.3	2	0.4	44	0.5
n-Butyl acetate	94	4.7	431	3.3	2	0.6	8	0.5	2	0.4	12	0.2
iso-Butyl acetate	--		--		13	3.6	46	2.6	2	0.4	15	0.2
Amyl acetate	3	0.2	22	0.2	--		--		--		--	
TOTALS	119	6.0	564	4.4	22	6.2	57	4.4	6	1.2	71	0.8

Note: 1=number of USTs; 2=volume of USTs in thousands of gallons

TABLE 2 (cont.)
MAJOR ORGANIC CERCLA SUBSTANCES STORED IN USTs

Chemical Groups	California				New York				CMA			
	1	%	2	%	1	%	2	%	1	%	2	%
Monomers												
Acrolein	--		--		--		--		15	2.7	787	9.0
Ethylene oxide	3	0.2	40	0.3	--		--		14	2.5	345	3.9
Styrene	33	1.7	340	2.6	1	0.3	6	0.3	13	2.4	305	3.5
Acrylonitrile	1	<0.1	20	0.2	--		--		9	1.6	52	0.6
Vinyl acetate	11	0.6	165	1.3	4	1.1	6	0.3	7	1.3	151	1.7
Vinyl chloride	1	<0.1	10	0.1	--		--		5	0.9	163	1.9
Methyl methacrylate	6	0.3	61	0.5	1	0.3	1	0.1	5	0.9	48	0.5
Vinylidene chloride	4	0.2	58	0.4	--		--		1	0.2	7	0.1
Propylene oxide	7	0.4	58	0.4	1	0.3	10	0.6	1	0.2	20	0.2
1-Chloro-2,3-epoxypropane	--		--		--		--		1	0.2	50	0.6
Allyl chloride	--		--		--		--		2	0.4	20	0.2
Ethyl acrylate	3	0.2	51	0.4	3	0.8	6	0.3	--		--	
TOTALS	69	3.6	803	6.2	10	2.8	29	1.6	73	13.3	1948	2.2
Miscellaneous Chemicals	145	7.4	951	7.0	21	6.0	144	8.0	48	8.8	452	5.0
Pesticides	37	1.4	598	4.2	--		--		--		--	
TOTALS	1979		12997		357		1725		549		8725	

Note: 1=number of USTs; 2=volume of USTs in thousands of gallons

TABLE 3
UST DESIGN CHARACTERISTICS

by percent

	New York	CMA
STEEL		
Carbon	86.4	87.7
Stainless	3.4	6.0
Double Wall	0.5	ND*
TOTAL	90.3	93.7
Concrete	3.4	3.5
Fibreglass	3.4	0.7
Copper		1.1
Aluminum		6.2
OTHERS	2.9	0.8

*ND - Not determined

U.S. EPA EVALUATION OF VOLUMETRIC UST LEAK DETECTION METHODS

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ABSTRACT

This report summarizes the quantitative results through January 12, 1987 of the ongoing U.S. Environmental Protection Agency's (EPA) Hazardous Waste Engineering Research Laboratory program to evaluate the performance of commercially available, volumetric test methods for detecting leaks in underground petroleum storage tank systems. Volumetric methods (i.e., those operating in or on the tank that yield a quantitative estimate of the leak rate) can be influenced by a wide variety of environmental factors, all of which can significantly reduce the accuracy of the measurement.

The first set of full-scale product temperature experiments on a 30,285 L (8,000 gal) tank were conducted to assess the impact of thermally-induced volume fluctuations on the testing of overfilled tanks, the most common test condition. The initial data indicate first that thermal effects are large when the temperature of the added product is different from that of the *in situ* ground and stored product temperature, even 24 h after product delivery, and second that these effects can significantly impair a method's ability to detect small leaks unless the thermally-induced volume changes are compensated. When the vertical and horizontal distribution of temperature was investigated, the results indicated that volume-weighted temperature changes measured by a single vertical thermistor array located at the fillhole of the tank would be adequate for compensation of thermally-induced volume changes of the product throughout the tank. The results also indicated that a 20 cm (8 in.) vertical separation of thermistors on the array was adequate to characterize the temperature fluctuations that caused these volume changes.

An estimate of the technological limits of detecting leaks with volumetric test methods is also being made. These results can be used to assess the performance of existing test methods, as well as new ones that might be developed in the future. The analysis suggests that, with proper instrumentation and procedures, a leak rate of 0.19 L/h (0.05 gal/h) can be detected with a probability of detection (PD) of 0.95 and a probability of false alarm (PFA) of 0.001, providing no other sources of ambient noise are present (e.g., tank deformation, vapor pocket).

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INTRODUCTION

Leaking petroleum underground storage tanks (USTs) represent a serious environmental threat. The United States Environmental Protection Agency (EPA) recently estimated that approximately 25% of the UST throughout the United States are leaking at a rate of 0.23 L/h (0.06 gal/h) or greater (1). Records from past release incidents indicate that, without the use of release detection, a release can become substantial before it is detected. Most releases are first detected by people seeing, test tasting, or smelling the released material in the environment. Only about 20% of the releases have been detected by inventory reconciliation or tank tightness testing procedures. The voluntary practice of release detection by UST owners and operators gives rise to the low percentage of incidents reported by release detection methods (2).

The 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of 1976 have charged the EPA with developing regulations for the detection of releases from UST. Development of technically sound and defensible regulations requires that the threat to the environment and the technological limits of release detection be known. The threat to the environment is extremely difficult to define because the transport, fate, and amount of petroleum considered hazardous in the environment are not sufficiently known. A performance standard that is based on the current technology will minimize the uncontrolled release of petroleum product. Unfortunately, the data required to formulate a realistic regulatory policy are incomplete or nonexistent. Many commercially available leak detection methods can be used to detect small releases. Claims of excellent performance are made, but little evidence, theoretical or experimental, is provided to support these claims. Most manufacturers of test methods claim to detect leak rates of 0.19 L/h (0.05 gal/h) or smaller, the practice recommended by the National Fire Protection Association (NFPA) Pamphlet 329 (3). Limited evidence suggests that the most common methods are not reliably meeting this claim (4).

The environmental hazards posed by uncontrolled releases from UST are so formidable that they require the systematic application of current and evolving release detection technology. The Hazardous Waste Engineering Research Laboratory (HWERL) is currently conducting a research program to characterize the performance of the commercially available volumetric tightness test methods and to determine the technological limits of detection using this approach. A detailed description of the project is presented in "Protocol For Evaluating Volumetric Leak Detection Methods for Underground Storage Tanks" (5). An overview of the approach, including a discussion of the major variables affecting volumetric leak detection methods and a description of EPA's full-scale, environmentally safe test apparatus, has also been published (6). Over 40 volumetric detection methods have been identified so far.

The purpose of this engineering research program is to evaluate commercial volumetric methods for detecting leaks in underground storage tanks containing petroleum motor fuels such as gasoline, kerosene, and diesel oil. The results will be used to develop regulations to reduce the pollution of groundwater by leaks from these tanks. This progress report briefly summarizes the important results to date derived from the experiments being conducted in the specially designed test apparatus located at the EPA's Hazardous Waste Engineering Research Laboratory (HWERL) facility in Edison, New Jersey. A complete research report will be published at the conclusion of this research project.

OVERFILLED TANK TEST EXPERIMENTS

The most common method of release detection is a volumetric tank tightness test. Product level changes in the tank are measured and converted to volume changes through the knowledge of the tank geometry. Product level measurements alone are not sufficient to detect a small leak, because the height changes that normally occur in a tank that is not leaking are large enough to mask a small leak. These volume changes can arise from expansion or contraction of the product in the tank by temperature changes, expansion or contraction of the volume of any trapped vapor by temperature and pressure changes, structural deformation of the tank ends and walls, evaporation or condensation of the product, and surface and internal waves. A method of compensating for each of these sources of ambient noise is required to detect small leaks.

Three classes of volumetric tank test methods are being evaluated: overfilled tank test methods, partially-filled tank test methods, and methods that circulate product in the tank. The most common method of tank testing is the overfilled tank test. This type of method tests the entire system (tank, piping, and associated underground equipment) for leaks, but requires the purchase of sufficient additional product to fill the tank system completely. For a low-budget operator, this requirement can impose a substantial financial hardship. It should also be remarked that many UST systems are never filled this full at any time during routine operations.

In this method, product is added to the existing product in the tank to obtain a level in the fill tube itself or in an above-ground extension of the fill tube. Accurate measurement of product level in the fill tube is easy; for example, a 0.04 L (0.01 gal) volume causes a 0.37 cm (0.15 in.) product level change in a system with a 10 cm (4 in.) fill tube with a 5 cm (2 in.) vent tube.

Ambient Noise

A comprehensive set of experiments is being conducted in the test apparatus to characterize and model the magnitude of each source of ambient fluctuations that limit the performance of volumetric leak detection test methods. The first tests focused on the volumetric fluctuations that limit the performance of test methods that overfill the tank. The dominant ambient volume fluctuations for these test methods are:

- expansion and contraction of the product in the tank by temperature changes,
- expansion and contraction of trapped vapor in the tank and piping by temperature and pressure changes, and
- structural deformation of the tank by changing product levels before or during the test.

Product level changes in overfilled tank test methods will be generated by summing the volume changes effected by these three sources of noise. Three types of experimental runs are being conducted to collect the data required to develop these three models and to validate them. This is accomplished by designing a set of experiments to isolate each noise source and show that the residual volume fluctuations, after subtracting the volume fluctuations predicted by the noise model from the measured product fluctuations, are small enough to be negligible (i.e., less than 0.04 L/h).

Product level changes due to evaporation or condensation are small because of the small surface area open to the atmosphere. Surface waves are essentially nonexistent, although a long period standing wave (seich) in the tank is possible due to multiple openings in the tank which may be vented to the atmosphere during a test. Internal waves in a tank will cause periodic temperature changes and sometimes periodic product level fluctuations that are unrelated to the temperature changes required to estimate thermal expansion or contraction of the product. These effects, which are characteristic of the temperature field, can be minimized by properly sampling and filtering the data.

Thirteen 24- to 48-h tests have already been conducted to characterize the temperature field and volume changes generated by temperature fluctuations. Each run has been conducted by adding 15,142 L of product to the half-filled 30,245 L capacity steel tank at temperatures that are 0 to 10°C cooler or warmer than the temperature of the ground, and of the *in situ* stored product. After adding product, all tests were conducted with the fluid level between 234 cm (92 in.) and 236 cm (94 in.) This level permits temperature changes in a full tank to be approximated accurately without trapping vapor pockets.

Product Temperature Analysis

Three analyses of data from these thirteen tests have been performed. The first analysis estimates and tabulates the magnitude of the thermal volume changes as a function of time after delivery. The results indicate that thermally-induced volume changes are large, even 24 h after adding product to the tank, and that temperature compensation is necessary to conduct an accurate tank test. In the course of a 24-h test, uncompensated volume rates of 1 to 3 L/h were observed.

The second and third analyses characterize the vertical and horizontal spatial inhomogeneities of the temperature field, respectively. The coefficient of thermal expansion, the volume of the product in the tank, and the temperature change of the product is required to estimate thermally-induced volume changes of the product. The second temperature study was performed to compare the ability of each of the three thermistor arrays to measure thermally-induced volume changes in the tank. In particular, this analysis examined whether one thermistor array is sufficient to characterize the temperature field of the whole tank. The data were analyzed as follows:

- o A thermally-induced volume change time series was generated for each thermistor array as well as for the average of the three arrays.
- o The average thermally-induced volume change computed for all three arrays was subtracted from each array's volume, and the residuals were differentiated and smoothed with a 1-h box car window (running average).
- o The root mean square (rms) error was calculated for successive 2-h segments to give an estimate of the error in a thermally-compensated leak rate determined from an individual array.

Results suggest that a single vertical array of thermistors having a spacing of 20 cm is sufficient to characterize the temperature field of the whole (2.4 m diameter by 6.1 m long) tank when testing is begun at least 4 to 6 h after product delivery. In the first 4 to 6 h, large differences in temperature between the three horizontally spaced arrays are observed; during this interval even three arrays are not sufficient to characterize the temperature field. However, after 6 h the measurements indicate that the difference in the temperature fluctuations between arrays is small.

The average rms errors for each array are summarized in Table 1. This analysis suggests that a single array can measure temperature changes to within 0.04 L/h, which is required to reliably detect leak rates of 0.19 L/h. Because of the turbulence caused by the physical disturbance of mixing and by the thermal settling of the fluid in the tank, the rms errors calculated for the first 6 h of each experimental run were excluded from the analysis. Due to the presence of a bad thermistor in the array, the rms of Array 3 appears to be somewhat higher than those of Array 1 or Array 2.

TABLE 1. AVERAGE RMS* ERROR FOR THREE VERTICAL THERMISTOR ARRAYS

Array 1	0.041 L/h
Array 2	0.039 L/h
Array 3	0.046 L/h
Mean	0.042 L/h

* Root Mean Square

The cumulative rms errors were plotted as a function of the time of day to observe any diurnal variations of the rms error. An increase of approximately 0.01 L/h in the rms error is observed during the 6 h period from 10 a.m. to 4 p.m., coinciding with the period of most rapid change of air temperature. For the next 18 h, the rms error settles to a level of approximately 0.038 L/h.

The third analysis was performed to investigate whether the 20 cm vertical separation of thermistors on each array was adequate to characterize the vertical distribution of temperature in the tank. The mathematical coherence was formed between adjacent pairs of thermistors and was found to be near unity for frequencies less than 1 cycle per 2 h.

These results have a significant implication for tank testing. First, temperature compensation is essential to the conduct of an accurate tank test. Second, independent of structural deformation effects, a waiting period of at least 4 to 6 h after topping off a partially filled tank with product is required before testing begins. Third, a single array of thermistors, at the fill hole, is sufficient to obtain the necessary data for effective temperature compensation. The effect of the number of thermistors, test time, and sample interval is being quantified by simulating the performance of six canonical test methods.

PERFORMANCE OF CANONICAL TEST METHODS

The performance of six canonical (representative) methods for testing overfilled tanks is being evaluated while detailed descriptions of commercially available methods are being collected and modelled. These "theoretical test methods" invoke sound operational, data collection, and data analysis practice. The implied practice can readily be incorporated into commercially available methods. This preliminary evaluation will support the development of performance standards sooner than would otherwise be possible. The canonical methods are described as follows:

- product level measurements only (no temperature measurements);
- product level and one temperature measurement at the center of the tank;
- product level and three temperature measurements, volumetrically weighted by tank volume, and located at three equally spaced vertical intervals;
- product level and five temperature measurements, volumetrically weighted by tank volume, and located at five equally spaced vertical intervals;
- product level and the average temperature computed from a vertical array of twelve equally spaced temperature sensors; and
- product level and a volume-weighted average temperature computed from a vertical array of twelve temperature sensors.

Performance will be expressed in terms of the probability of detection (PD) and probability of false alarm (PFA). PD is the probability that a given method will detect an actual leak at or above its threshold rate in an UST. PFA is the probability that a given method will declare that a tank is leaking at or above its threshold rate when, in fact, the tank is tight.

The data for each test method are collected and processed at a 1 sample/min rate. The precision of the height measurement sensor is assumed to be 0.25 mm (0.01 in.), corresponding to a volume change of 0.002 L (0.0005 gal). The temperature sensor precision is taken to be 0.001°C. All tank tests are conducted between 12 and 24 h after product delivery to a half-filled tank. The estimated volume rate for each tank test is calculated by subtracting the temperature time series from the product level time series after converting each to equivalent volume, and fitting a least squares line to the residual volume.

Preliminary performance curves that display PD versus PFA as a function of leak rate have been generated for each canonical method and for test periods of 1, 2, 3, and 4 h. The curves are generated from a histogram of the temperature compensated volume fluctuations compiled using the data from the EPA test apparatus. Typical results of these analyses are shown in Figure 1 for a canonical method employing five equally spaced thermistors in a single array. The results presented in this figure include only the volume fluctuations from one source of ambient noise (thermal expansion or contraction of the product). The performance results indicate that temperature compensation is essential and that performance is improved with increased test time and number of thermistors used for temperature compensation. Without temperature compensation, only leak rates of at least 4.75 L/h (1.19 gal/h) are detectable with a PD = 0.95 and a PFA = 0.001.

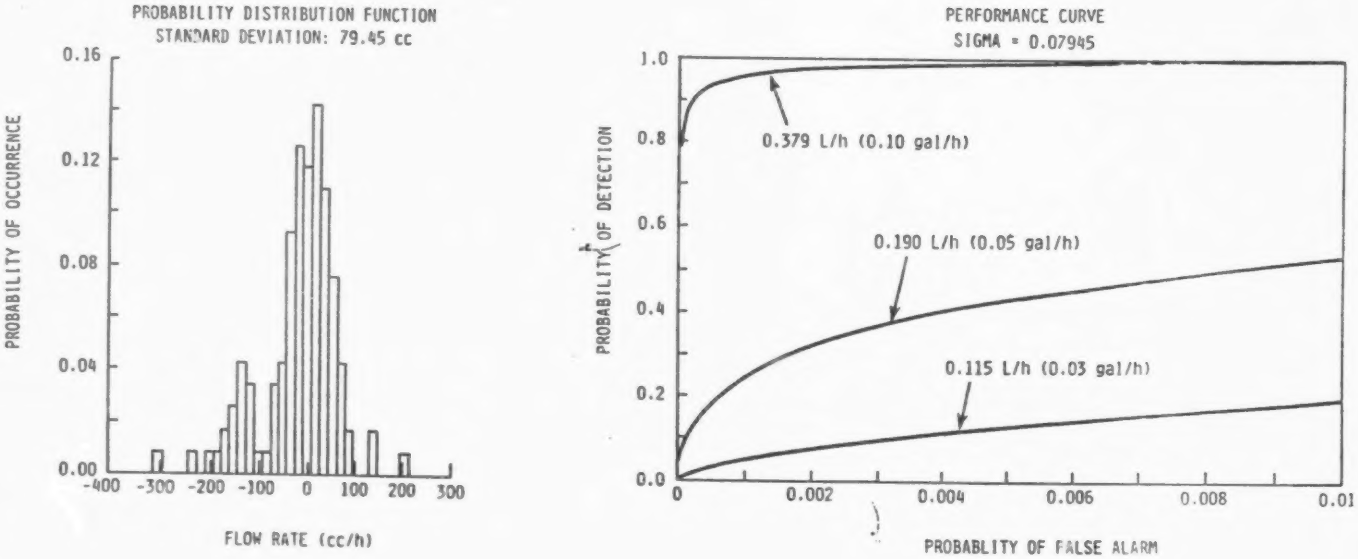

FIGURE 1 THE (a) HISTOGRAM AND (b) PERFORMANCE CURVE FOR A 1-h TEST OF THE CANONICAL TEST METHOD WERE OBTAINED USING FIVE EQUALLY SPACED, VOLUMETRICALLY WEIGHTED TEMPERATURE MEASUREMENTS. ONLY THE AMBIENT NOISE EFFECTS OF THERMAL EXPANSION AND CONTRACTION OF THE PRODUCT WERE INCLUDED IN THE ESTIMATE. THE DATA FROM TABLE 2 WERE USED IN THE ANALYSIS. RELIABLE PERFORMANCE IS OBTAINED FOR LEAK RATES GREATER THAN 0.379 L/h (0.10 gal/h).

The improvement in test method performance when the volume fluctuations are temperature compensated is reflected in Table 2. From this it can be seen that a 1-h test with a single thermistor compensation scheme will detect a leak rate of 0.42 L/h (0.11 gal/h) with a PD = 0.95 and a PFA = 0.001. A 2-h test, however, with temperature compensation provided by a complete vertical array that has been volumetrically weighted, will detect a leak rate of 0.17 L/h (0.04 gal/h) at this performance level.

Tests are currently under way to quantify the magnitude of the volume changes caused by structural deformation of the tank and by trapped vapor in the tank. When these are complete and more temperature runs are added to the data base, a final performance estimate can be made. These results should be indicative of the performance that the technology is capable of achieving.

As part of the experiments completed to date, a method of measuring the volume of trapped vapor pockets in any UST has been developed to afford estimates of volume fluctuations produced by a vapor pocket. This is an important measurement because all overfilled tanks trap vapor, and heretofore there has been no means to measure the volume of these pockets. With all proturberances removed, the tanks of the test apparatus trap approximately 40 L of vapor when overfilled. These tanks were installed with end to end elevation changes of less than 0.6 cm. Field installations have a typical elevation difference of 5 cm and will, therefore, trap larger volumes of vapor. As a consequence, the 40 L of trapped vapor represents a very much smaller volume of trapped vapor than is typically found in the field.

TABLE 2. DETECTABLE LEAK RATE IN LITERS PER HOUR FOR THREE OF THE CANONICAL TEST METHODS FOR A PROBABILITY OF DETECTION OF 0.95 AND A PROBABILITY OF FALSE ALARM OF 0.001. (This performance estimate includes only the volumetric fluctuations caused by product temperature fluctuations. A 0.05 gal/h leak rate is equal to a 0.19 L/h leak rate.)

	Leak Rate (L/h)			
	Test Duration			
Canonical Test Method	1-h	2-h	3-h	4-h
One Thermistor	0.42	0.37	0.34	0.33
Five Thermistors	0.38	0.31	0.28	0.27
Vertical Array, Volumetrically Weighted (12 Thermistors)	0.32	0.17	0.13	0.12

CONCLUSIONS

Preliminary results from the first set of ambient noise experiments in the test apparatus are available. These early tests have been conducted to assess the impact of temperature fluctuations on testing in overfilled tanks (the most common condition for volumetric testing). The initial results indicate that product thermal effects are large when the temperature of the added product is different from that of the *in situ* ground and the stored product. During the time period immediately after product addition (i.e., the first 4 to 6 h), the temperature fluctuations are not horizontally coherent, so that a single thermistor array cannot adequately compensate for thermal fluctuations. After this initial period, the horizontal coherence of the long term trends is of order one, and a single vertical array of thermistors at the fill-hole of the tank can provide adequate thermal compensation. Coherence analysis between pairs of thermistors separated vertically by 20 cm indicates that this separation is generally adequate to define the vertical temperature distribution of the temperature field in the tank.

At the same time the experimental work was being carried out, a theoretical basis was developed that EPA's Office of Underground Storage Tanks (OUST) could use to rapidly assess the performance of existing test methods, as well as the performance of any newly developed tests that might be brought to EPA's attention in the future. When presently available commercial volumetric leak detection tests that overfill the tank were examined, the majority were found to fall into six classes. For each of these

ACKNOWLEDGMENT

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2.

NATO/CCMS PILOT STUDY ON DEMONSTRATION OF REMEDIAL ACTION TECHNOLOGIES FOR CONTAMINATED LAND AND GROUNDWATER

by

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ABSTRACT

Groundwater and soil contamination by hazardous waste is a pervasive problem in industrialized countries. As scarce resources, water and land must be returned to productive use. Current cleanup efforts are hampered by limited technology options and high costs. It's desirable to build up the knowledge base so that more efficient, cost effective remedial technologies can be developed. However, the urgent needs of society require that near-term solutions be found and applied to the most significant pollution problems. Consequently, promising new technology must be tested and demonstrated to determine their applicability and effectiveness for today's problems.

The U. S. Environmental Protection Agency has established a formal program to enhance the development and use of new or innovative technologies for mitigating the problems caused by releases of hazardous substances at uncontrolled hazardous waste sites. In the United States the program is called the Superfund Innovative Technology Evaluation or SITE Program.

In November 1986 the NATO-CCMS formally adopted a U. S. proposal for a new pilot study entitled "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater." The following NATO countries opted to participate:

- Canada
- Denmark
- Federal Republic of Germany
- Greece
- Italy
- The Netherlands

- Norway
- Spain
- United States

Two non-NATO countries, Australia and Japan have also expressed an interest in participating.

The purpose of this new study will be to field demonstrate and evaluate new technology and/or existing systems for remedial action at uncontrolled hazardous waste sites and is a logical international extension of the U. S. EPA, SITE program. This study will offer the potential to obtain a multiple data base on various remedial action unit processes, that is microbial degradation, on site treatment/destruction, fixation, without any single country having to commit a disproportional amount of its internal resources to a specific research activity.

Simultaneously, along with the primary demonstration portion of the study, the opportunity for long term technology transfer of environmental restoration technology development will be provided to participating countries.

INTRODUCTION

The first working group meeting was hosted by the Federal Republic of Germany on March 16-20, 1987. At this meeting experts from six countries (Canada, Denmark, Federal Republic of Germany, the Netherlands, Norway, and U.S.A.) agreed on an initial program of 12 demonstrations of technologies to clean-up contaminated soils and groundwater.

The sites were selected by a majority vote of all participating countries (no country was permitted to vote for its own sites) after agreement that each interested country would have at least one site automatically accepted. With this in mind, every attempt was made to maximize diversity within the limits of the 21 sites from which selections were made. Special emphasis was placed on the diversity and innovative aspects of the technologies. Each project is expected to have a substantial data base on its application within the 1987 calendar year.

The International Study Group will meet twice yearly to review progress on each demonstration project and to consider the inclusion of further projects in the program. The results of the various projects will be published in a final "state-of-the-art" report on treatment technologies for contaminated land and groundwater by Plenum Press as an official NATO report. Interim reports will be published in international journals from time to time as available data warrants.

Discussion:

Table 1 is a summary of the technologies accepted for the first year of the study classified by country.

Further details on the sites can be obtained from the individual referenced sources. It is important to note that substantial results are not yet available on any of the sites as the overall study (NATO-CCMS) was only approved in November of 1986 and the sites selected in March, 1987. Twelve site remediation projects from six countries were selected for the first phase of this multi-year information exchange project. The projects can

TABLE 1. NATO-CCMS Pilot Study on Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

Country	Summary of Technologies
Canada	° Groundwater treatment
Denmark	° Groundwater treatment and aerobic/ anaerobic biological treatment
Germany	° Groundwater treatment, cleaning, and thermal treatment
Japan	° Thermal treatment followed by calcination and mercury recovery
Netherlands	° Thermal treatment in consort with biological treatment ° In-situ biorestoration ° Landfarming
United States	° Electric infrared incineration ° In-situ biodegradation ° In-situ soil vapor extraction

be grouped by the type of technology into the following:

- 4 in-situ biological treatment (Denmark, Germany, Netherlands and U.S.A.)
- 3 thermal treatment (Germany, Netherlands and U.S.A.)
- 2 groundwater treatment (Canada, Denmark and Germany)
- 1 high pressure soil washing (Germany)
- 1 land farming (Netherlands)
- 1 soil vapor extraction (U.S.A.)
- 1 chemical treatment (Japan)

Some of the sites have more than one technology to be demonstrated.

Canada(1)

Canada has one site included in the study. The Ville Mercier site is in a small community located on the south shore of the St. Lawrence River, about 20 km southwest of the city of Montreal. Groundwater is a significant source of supply for the potable water needs of the local population.

From 1968 to 1972, some 40,000 m^3 of waste oils and liquid industrial wastes from chemical and petrochemical industries in the Montreal area were dumped into a lagoon in an old gravel pit located several kilometres southeast of Ville Mercier. In October 1971, it was discovered that several wells in the vicinity were contaminated. The dump site was closed in 1972, and it was estimated that 20,000 m^3 of wastes remained in the lagoons. Sampling conducted by the Quebec Ministry of the Environment (MENVIQ) revealed the presence of phenols and chlorinated organic compounds in the groundwater in the area. Subsequent studies indicated that approximately 30 km^2 of the aquifer had become contaminated.

Four specific zones of contamination were delineated. The first two, where the groundwater was highly contaminated, occurred within 2 km of the source. More than 80 organic compounds were identified in zone 1. The principal contaminants were phenols, trichloroethylene, dichlorethane, trichloromethane, trichloroethane, chlorobenzene, dichloroethylene and Arochlor 1254. Two other zones of lesser contamination were delineated with a total areal extent of contamination estimated at about 30 km^2.

In addition to the inconvenience caused to the population and the loss of a water resource to thousands of people, the direct cost in this case of groundwater contamination may reach ten million dollars (Cdn) or eight million U.S.

A program to rehabilitate the aquifer was started by the Government of Quebec in 1981. The liquid material which was stored in the lagoon was first removed (incineration, landfill) in order to prevent additional contamination of the groundwater. Following this, MENVIQ awarded contracts to develop a purge-well system and to design and construct a groundwater treatment facility.

The pumping system consists of three (3) extraction wells located a few hundred meters downstream of the hazardous waste dump site. These wells create a cone of depression into which contaminated groundwater is drawn, i.e., it forms a hydraulic trap.

Denmark(2)

Denmark has one site included in the study. The Skrydstrup special deposit site was formerly a gravel pit which was later used for the disposal of chemical/industrial waste. Some of this waste was stored in several hundred drums at the site. There has been extensive chemical, geological and hydrogeological investigations conducted at Skrydstrup since 1986. Trichloroethane, trichloroethylene, paint and acid wastes have resulted in groundwater pollution. The remedial action will consist of digging up, removal and off-site disposal of several hundred drums, followed by groundwater pumping and treating and on-site aerobic/anaerobic biological treatment of the polluted soil. This remedial action is active at the current time.

The remedial action program of the Danish National Agency of Environmental Protection will involve 4 actual sites where remedial actions are enforced by the environmental authorities and is budgeted at 3,890,000 DKK or about $220,000 U.S.

Federal Republic of Germany(3)

The FRG has 3 sites included in the study, they are as follows:

° The Pintsch-uil Site(3) - is located in an industrial estate of West Berlin. The recovery of used oils has been carried out since 1924. Residual products were left in several pits and subsequently seeped into the soil and groundwater. After initial inspection of the company in 1976 the water authorities in charge directed that groundwater samples be taken. Based on the considerable pollution detected in the groundwater, it was directed that a supplemental project be initiated with the objective of groundwater sanitation.

In the autumn of 1984 a pilot plant to purify the contaminated groundwater was planned. The objective of this plant was to compile techniques of groundwater purification adapted to the special contamination detected here. The construction of this plant was entrusted to Messr. Harbauer, Engineering Office for Environmental Technology, Berlin.

At first the site was thoroughly investigated and then 3 clearing wells, having a maximum capacity of 40 m^3/h at 25 m WC, were first designed.

A preliminary pollutant analyses of groundwater samples indicate extensive contamination with a wide variety of organic compounds. Results showed concentration for:

hydrocarbons	up to	16,000 mg/l
oils	up to	1,000 mg/l
phenols	up to	225 mg/l

In addition to the dissolved and undissolved oils and their compounds, groundwater contamination is primarily caused by volatile organic compounds (VOCs), and chlorinated hydrocarbons. The analytic measuring values were the basis for the construction of a pilot plant to purify ground and seeping water on site.

This pilot plant has a capacity of 40 m^3/h and consists of oil separator, flotation, counter-current desorption with exhaust purification and active carbon purification.

Another major part of this remedial activity will involve full-scale cleaning of the contaminated soils scheduled to begin in March 1987. No data are currently available on this part of the clean-up effort.

° The scrap metal site in the Charlottenberg area of Berlin(3) is contaminated with cyanide, arsenic, cadmium, mercury, PCB, lead, volatile chlorinated hydrocarbons, and oil. Remedial operations have been active since December, 1986 and consist of high pressure soils washing. A Netherlands company, Klockner Oecotec GMHB, has used this high pressure soils washing process to clean 100,000 tonnes of contaminated soils and removed over 95% of the pollutants. High pressure water jets are used to physically strip off hydrocarbons and heavy metal residues from the soils. This process is particularly promising for sandy/gravelly soils but is less effective for clays.

° The coke oven site at Unna-Boenen, Notherhine, Westphalia is contaminated with aromatic hydrocarbons , tars and acid resins. Volatile organic compounds comprise 5% of the waste, by weight. The site is estimated to be 230,000 square meters in area. It represents a number of similar sites throughout the FRG.

A variety of technologies will be applied to the site, individually focused on the soil and aqueous phases of the contamination. A 50 ton per hour, transportable thermal unit will be used to process the soil and redeposit it on-site. The unit has been successfully pilot tested on similarly contaminated soils at a 7 ton per hour rate with a destruction effectiveness of approximately 98%. In addition, in situ enhanced indigenous microbial degradation is underway, using nitrate as an electron acceptor. For contaminated water, a combination of air stripping, flocculation, sedimentation and filtration are under consideration.

The Netherlands(4)

The Netherlands has 3 sites included in the study, which are as follows:

° The contaminated soil at the former gasworks site in the Province of Zurd, Rotterdam, will be excavated and transported to the thermal destruction installation of Ecotechniek. The soil is contaminated primarily with polynuclear aromatics (PNA's) and complexed cyanides (ferri-ferro cyanides) caused by spillages and dumping of waste materials. The installation of Ecotechniek B.V. has been selected for evaluation because it has the highest 'production' of cleaned soil in the Netherlands (over 300,000 m^3). Although the installation has proven to be applicable in that it removes and destroys many types of contaminants (oil, PNA's, aromatics, cyanides) from soil, there is a need to assess more accurately the relation between type of contaminated soil, process conditions and treatment results (including air emissions).

The installation consists primarily of an internally heated rotating kiln (direct heat transfer) and an afterburner for the off gases; these operate at a maximum temperature level of 550°C and 1100°C respectively.

Main purposes of the demonstration project are:

a. Evaluation of the treatment results of the above described thermal installation for cleaning of soil from a former gasworks site.
b. To obtain insight into the start-up and reliability problems at or about $115,000 U.S. soil treatment plants in a general sense.

The evaluation which is planned to start in May 1987. The evaluation follows the approach developed by ('A Standard Method for Evaluating Soil Decontamination Techniques - a First Outline'). It is planned to evaluate the installation during periods of two days each, in which fluctuations in process conditions and type of contaminated soil should be kept at a minimum.

Three periods will be evaluated:

1. Normal (or standard) process conditions and moderately contaminated soil
2. Normal process conditions and highly contaminated soil
3. Deviating process conditions (high temperature) and moderately contaminated soil.

In all cases use is made of soil with a rather high peat (humus) and clay content.

During the evaluation attention will be given to:

° Gaseous emissions (C_xH_y, HCN, SO_2, NO_x, dust)

° Characteristics of the contaminated soil (feed) and the cleaned soil (product), such as particle size distribution, free-CN, total-CN, PNA's, aromatics. Depending on the homogeneity of feed and product, 8 to 20 soil samples will be analyzed. The soil samples will also be subjected to leaching tests and bioassays.

° The Asten Site in the province of Noord-Brabant is a petro (gasoline) station, where the soil is contaminated with petro containing small amounts of lead, and a small quantity of diesel oil. The contamination is caused by a leaking tank of the petrol station. At least 30,000 liters of normal gasoline have leaked and about 400 cubic meters of soil have been contaminated.

This project is aimed at optimizing the treatment of deeper layers of contaminated soil by enhancing in situ microbial activity. The development of in situ techniques is important for the reclamation of other sites similar to gasoline stations. It is expected that the use of this technique will result in cost reduction since it will avoid costs for excavation and allow the petrol station to continue its operation.

The project is being carried with the cooperation of the RIVM (National Institute of Public Health and Environmental Hygiene) and the TNO (Netherlands Organization for Appled Scientific Research). Funding support is provided by the Ministry of VROM (Housing, Physical Planning and Environmental Hygiene).

° The third site submitted by the Netherlands is the Wijster site in the province of Drenthe. This site is the former location of a waste disposal company. The primary emphasis will be on improving landfarming methods for the bio-destruction of gasoil, crude oil and halogenated hydrocarbons (for example, hexachlorocyclohexane).

Contaminated soil will be excavated and spread over a drained sand bed. The sand bed will be isolated from the subsoils by a plastic membrane. Nutrients will be added and the contaminated soils will be covered by an oxygen permeable plastic membrane or plants to prevent erosion.

Japan(5)

Japan has one site included in the study. Because no representative from Japan attended the March site selection meeting, this activity must still be considered tentative. Until confirmation is received from the Japanese Environmental Agency - National Institute of Environmental Studies - discussion on their site will be limited to reporting that it's a former electro-chemical industry site where the remedial action will involve thermal/ chemical treatment and recovery of mercury in contaminated soils.

United States(6)

The U.S.A. has three sites included in the study. They are as follows:

° Peak Oil, Tampa, Florida. The Peak Oil site is a former facility used by an oil re-refiner. A former waste lagoon contaminated with oil re-refining waste containing PCB's and lead is contaminating the local groundwater supply. The facility has been inactive. In 1984, investigation began to characterize the type and extent of cleanup.

Remedial investigations conducted at the Peak Oil site determined that the waste lagoon was a source of PCB and lead contamination. Because of contamination to the local groundwater supply, it was necessary to remove the source of contamination. The soil in the area is sandy and the groundwater table is very near the surface. The lagoon has been drained of water and sand, soil and lime have been mixed with the lagoon contents to further adsorb any water and neutralize the acidic waste. The lagoon was contaminated with acetic acid that was used in the re-refining process. These materials were mixed in place by a bulldozer to obtain a homogeneous, dry material. The level of PCB's measured was less than 50 ppm. Lead has been measured at 10-15 ppm.

Based upon the waste and the oil-soil matrix present at the site, thermal destruction technology was selected for the cleanup of the waste lagoon. In May of 1986 the Shirco Infrared Systems pilot incinerator was brought to Peak Oil for a test burn of the PCB contaminated soil. This test indicated that the Shirco infrared technology was an acceptable thermal destruction technology for the waste present at this site.

The infrared incineration system consists of a continuous conveyor belt furnace with associated material feed and discharge systems, process control and instrumentation equipment, emission control systems, and heating element power center. This system is mounted on transportable trailers. Hazardous material is conveyed to the furnace as sludges or solid wastes. The feed material drops onto a metering conveyor located at the feed end of the furnace. The metering belt is synchronized with the furnace conveyor screw which distributes the material across the width of the metering belt. Material enters the furnace through a rotary airlock.

The material then moves through the furnace where it is exposed to infrared radiation in multiple temperature-controlled zones. Zone temperatures are controlled by varying the input power (electric) to maintain preset zone setpoint temperatures. As the material moves through the furnace on the belt, it is exposed to the thermal environment necessary for oxidation of volatiles and solid organics. This technology is primarily applicable to solids, sludges and contaminated soils. The technology is also applicable to both organic and inorganic waste streams.

- Eglin Air Force Base. This jet fuel spill site is near the city of Fort Walton Beach in Florida. In 1984 a large area of dead grass appeared in the base petroleum storage area. The smell of fuel indicated that an underground fuel leak had occurred. Pressure testing of underground fuel lines revealed the source of the spill, a one liter per minute leak in a 15 cm diameter pipeline. The duration of the leak is unknown; however, soil and groundwater sampling indicates that as much as 100,000 liters of jet fuel have contaminated 6000 - 8000 cubic meters of soil and shallow groundwater.

After the spill was discovered, local authorites characterized the extent of contamination and established a series of shallow trenches to recover the free product. During 1985 over 30,000 liters of jet fuel were recovered using skimmer pumps. In October of 1986, the Air Force Engineering and Services Laboratory initiated a full-scale research project at the site to study enhanced biodegradation methods for removing fuel residuals from soil and groundwater.

Surface and underground spills of jet fuel are the most common source of soil and groundwater contamination at U. S. Air Force bases. As a result, the Air Force Engineering and Services Laboratory is investigating cost effective methods for decontaminating fuel saturated soils and impacted groundwaters. In-situ biodegradation provides a method of eliminating fuel residuals from the unsaturated zone and removing a long-term threat to the groundwater.

The degradation of petroleum hydrocarbons has been extensively studied over the last 25 years and is well understood in the laboratory. However, extensive data on full-scale field studies is seldom available or published and much of the experience rests with experts who have a financial interest in the technology. The goals of this site demonstration will be to generate new data on the in-situ degradation of specific jet fuel components, to optimize nutrient/oxygen additions, and to maximize contact between nutrients, soil microbes and fuel soaked soils. The study will be conducted over a two-year period to provide information on the lower limits of biological removal of fuel compounds. A control area has been established in a fuel contaminated area on the upgradient end of the site. The purpose of this control area will be to compare natural levels of degradation to the enhancement provided by nutrient/oxygen additions.

The total cost of this site demonstration is $780,000. Of this total, approximately 50% is for design and operation of the system, 25% is for sampling and analysis, 15% is for nutrients and hydrogen peroxide and 10% is for well installation and delivery equipment. More precise cost information will be available when the project is fully operational.

- Vernona Well Field. The Verona Well Field site consists of several distinct contaminated areas within approximately 100 acres. The well field itself contains 30 production wells that supply the entire city of Battle Creek, Michigan, including several major businesses. The site also includes a railroad marshalling yard and two solvent facilities. The Thomas Solvent Raymond Road (TSRR) facility is a former solvent repackaging and distribution facility. Solvents were stored in 21 underground storage tanks which were later discovered to be leaking. The TSRR facility is located about one mile upgradient of the well field. It is primarily a residential area surrounded by a few businesses.

The contamination problem at the Verona Field site was first discovered in August 1981, during routine testing of the city's water supply. Volatile organic compounds (VOCs) were discovered in 10 of the production wells. An area-wide survey by the U. S. EPA Technical Assistance Team (TAT) in the Spring of 1982 determined that the TSRR facility was a potential major source of well field contamination. This was confirmed during remedial investigation activities. Chlorinated hydrocarbons are the most significant environmental contaminants. Groundwater and soil contamination within the TSRR facility was found with VOCs as high as 100,000 and 1,000,000 ppb respectively. The total estimated mass of organics in groundwater and soil at TSRR was 440 lb. and 1,700 lb., respectively.

A two-stage approach to remedial action at the TSRR facility was adopted. Each assembled remedial alternative evaluated included separate but related alternatives for groundwater and soil. The selected alternative for the site includes a groundwater extraction (GWE) system in conjunction with a soil vapor extraction (SVE) system. Due to the significant mass of contaminants in the soil, alternatives that employed both groundwater and soil remediation were developed. Several alternatives for soil cleanup were evaluated, including SVE, excavation with on/off-site disposal, site capping, soil washing (saturating the unsaturated zone with water extraction), and no action.

The key components of the SVE system are extraction wells screened primarily in the unsaturated zone and a vapor phase activated carbon treatment vessel. The entire system will be closed (piping will lead directly from the extraction wells to the carbon system). A performance goal of 10 ppm total VOCs in the unsaturated zone was established. At present, eight extraction wells are envisioned. Due to the innovative nature of the SVE system, the U.S. EPA has adopted a formal two-step procurement approach for both SVE design and construction. Technical proposals for the design will be solicited, then cost proposals will be evaluated only for those bidders submitting acceptable technical proposals. However, at a minimum, five extraction wells followed by vapor phase carbon treatment will be part of the system.

Summary and Conclusions

The NATO-CCMS pilot study program provides an excellent forum for an international exchange of current, state-of-the-art, scientific information pertinent to environmental protection. One of the challenges in modern society is dealing with the byproducts resulting from manufacturing. Throughout the world, improper handling and disposal of hazardous materials and hazardous waste has caused both groundwater and soil contamination. This is especially true in industrialized countries. Water and land are scarce resources, and must be returned to productive use. Current cleanup efforts are hampered by limited disposal sites, and high cost. It has not been proved that land disposal, particularly landfilling of hazardous waste, is effective over the long term in containing hazardous wastes. Immediate solutions must be found and applied to the most serious pollution problems. Promising new treatment technologies must be tested and then demonstrated to see if they apply to, and will be effective for today's pollution problems. We must build a knowledge base so that more efficient, cost effective remedial technologies can be developed. This knowledge base must include "lessons learned" from the past. A knowledge of technical and economic limitations, or failures, of the various technologies is as beneficial as the details of successes. Through the exchange of information on emerging remedial technologies, nations may pool their knowledge and experience and make the best use of their own limited resources.

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3. Werner, W., 1987 "The Sanitation of the Pintsch Site," Harbauer & Co., Ingenieurboro fur Umwelttechnik, Bismarckstrasse 10-12, 1000 Berlin 12, Federal Republic of Germany.

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Site 2 - Scrap metal site at
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REACTIVITY OF VARIOUS GROUTS TO HAZARDOUS WASTES AND LEACHATES

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ABSTRACT

A laboratory study was conducted to evaluate the potential of selected grouts for controlling the percolation of leachates from hazardous solid waste landfills or hazardous waste ponds. In the course of the study, seven different grouts were subjected to permeability tests and three of the grouts were tested for their reactivity by an immersion type test. Eight different chemicals, some with two concentrations, and two real-site wastes were used as permeants in the permeability tests, and as liquids for the immersion baths.

Of the seven grouts, the acrylate, cement-bentonite (mix 2), and urethane grouts had the lowest baseline permeabilities with water, ranging from 2.3×10^{-10} to 3.6×10^{-9} cm/sec.

During permeability testing with chemicals, the acrylate grout exhibited excellent resistance to the paint and refinery wastes, 25% acetone, 25% methanol, and sodium hydroxide, performed satisfactorily with cupric sulfate, ethylene glycol, and xylene, and was seriously damaged by aniline, 100% acetone, hydrocholoric acid, and 100% methanol.

The permeability of the cement-bentonite (mix 2) grout was tested with acetone, aniline, cupric sulfate, hydrochloric acid, methanol, and sodium hydroxide. With every one of these chemicals the permeability of the grout improved, ultimately reaching a practically impervious state.

The urethane grout maintained its low permeability with acetone, aniline, ethylene glycol, methanol, paint waste, refinery waste, and hydrochloric acid and it performed marginally well with cupric sulfate. However, the urethane lost its low permeability with sodium hydroxide and xylene.

Based on the comparision of permeability and reactivity test results, a scheme was proposed to correlate the permeability changes of grouts to the weight and consistency changes that may occur during their reactivity testing.

INTRODUCTION

One of the major environmental problems facing the nation is the threat of contamination of groundwater from leaking hazardous waste landfills and leachate ponds. If a waste site is underlain by an impervious stratum, the most cost-effective remedy may be using a cutoff slurry wall constructed around the site and keyed into the aquiclude. However, if there is no impervious stratum below the waste, the remedy may be the construction of a bottom seal created by injection grouting, in conjunction with a vertical slurry wall. Alternately, both the bottom seal and side wall may be made by injection grouting.

Injection grouting has been used for many years for stabilizing soils, to provide cutoff curtains under dams, for stabilizing tunnels, and more recently it was proposed for containment of hazardous waste (2,3).

When constructing an impervious barrier by injection grouting under a waste site, the grout must thoroughly penetrate the soil. After expelling the waste from the voids the grout must set and harden in the soil. In addition, the hardened grout must provide a durable impervious seal even when permeated by hazardous leachate.

The purpose of this study was to test the permeability and reactivity of selected grouts with ten chemicals to determine if the grouts had the durability to withstand the typical hazardous waste site environment, and thus could be considered for horizontal seal construction.

The permeability test results indicate that certain grout-chemical combinations caused the deterioration of the permeability of the grout, while others resulted in little or no detrimental changes. The reactivity test results show what effect chemical baths had on grout samples; some combinations caused weight gains, others weight losses, and still others caused no changes. In addition, changes in sample consistency were observed. The combined analysis of the two tests resulted in correlations that allow prediction of permeability changes from reactivity test results.

MATERIALS AND METHODS

All permeability tests and most reactivity tests were conducted on grouted soil samples. The permeability testing was conducted in specially constructed permeameters and safe environmental boxes, using selected chemicals as the permeants. The reactivity samples were tested by their immersion in selected chemical baths.

Grouts

In the typical batch of the cement-bentonite (mix 1) grout 3000 g Type III cement, 120 g bentonite, and 6000 ml water was used, resulting in a water-cement ratio of 2.0. The batches of cement-bentonite (mix 2) grout were made up of 3000 g MC-500 microfine cement, 120 g bentonite, 30 ml dispersant, and 2250 g water, yielding a water-cement ratio of 0.86. For ease of injection, pea gravel was used as the soil with both grouts.

The sodium silicate grout selected was SIROC 132, distributed by Raymond International, Inc. It consisted of 60% modified silicate, 25% water, 10% formamide, and 5% calcium chloride. A fine Mason's sand was used as the soil to avoid syneresis. Later extensions to the work included a glyoxal-modified sodium silicate grout and a sodium aluminate-modified sodium silicate grout in order to reduce the permeability of these grouts.

The urethane grout selected was CR360, a product of the 3M Company. A mixture of 89.2% water, 5.7% CR361 (gel inhibitor), and 5.1% CR360 (urethane polymer solution) was chosen. A silica sand was used with this grout.

AC-400, distributed by Avanti International, was chosen to represent the acrylate grouts. A mixture of 73.44% water, 24.99% AC-400, 0.74% triethanolamine (catalyst), 0.74% ammonium persulfate (initiator), and 0.074% potassium ferricyanide (inhibitor) was used. Silica sand was used as the soil.

Grouting Procedure

The soil samples for the permeability tests were pressure grouted in a 75 mm inside diameter plastic mold. Sample lengths could be varied as required. At least two pore volumes of grout were passed through the samples before completing the grouting process.

The 25.4 mm diameter by 25.4 mm high cylindrical reactivity samples were prepared in acrylic molds by first placing the sand in the molds and tamping the surface to densify it. The grout was then injected continuously from the bottom of each sample using a syringe. The cement-bentonite grout was poured into the molds, since these samples were prepared without a soil.

Permeameters

The permeameters used were flexible-wall type, specially built in-house to resist the chemicals and grouts. The elements in contact with the chemicals were made of one of the following: nylon, stainless steel, PVC or teflon.

Permeability Measuring Apparatuses

The percolation of the leachates through the grouted soil samples was performed in two permeability apparatuses that were housed in vented boxes utilizing a one-pass air system to remove any hazardous vapors. They had a total capacity of thirty testing stations. Each station had regulated chamber and driving pressures, and means to measure either leachate outflow only, or both inflow and outflow.

Permeability Testing

Since the main objective of the study was to investigate the effect of the various chemical leachates on the permeability of the grouts and compare them with permeabilities established with water, the first step was to permeate the samples with deionized water until equilibrium baseline permeabilities were reached. After that, the samples were permeated with their respective chemical leachates until an equilibrium permeability was established and a minimum of 2.0 pore volumes of chemical had passed through each sample.

Reactivity Testing

ASTM Standard C267-82 "Standard Test Method for Chemical Resistance of Mortars, Grouts and Monolithic Surfacings" was followed as guidance for the preparation, weighing, measuring and immersion of the specimens in the selected chemicals. Observations and weighings were made after 1, 7, 14, 28, 56 and 84 days of immersion. Plots were made illustrating the percent change in weight versus time for each sample and replicate series.

Chemicals and Hazardous Leachates Used

For this study, ten representative chemicals were selected. Eight of these organic and inorganic compounds represent a particular functional group as set forth in (3), and consisted of acetone, aniline, cupric sulfate, ethylene glycol, hydrochloric acid, methanol, sodium hydroxide and xylene. In addition, a real-site refinery waste and a real-site paint waste were included in the testing program, which were obtained as leachates from lysimeter studies conducted at the Center Hill Solid and Hazardous Waste Research Facility (1).

The chemical concentrations used were: acetone (100% and 25%), aniline (100%), cupric sulfate (20% and 10%), ethylene glycol (100% and 25%), hydrochloric acid (1N and 4N), methanol (100% and 25%), sodium hydroxide (25% and 10%), and xylene (100%). The real-site wastes used were unaltered.

RESULTS AND DISCUSSION

Permeability Test Results With Water

Three of the grouts tested had very low baseline permeabilities with water: acrylate ($k = 5.1 \times 10^{-10}$ cm/sec), cement-bentonite (mix 2) ($k = 2.3 \times 10^{-10}$ cm/sec), and urethane ($k = 3.6 \times 10^{-9}$ cm/sec). The other four grouts tested had permeabilities with water that exceeded 1×10^{-7} cm/sec.

Permeability Test Results For Acrylate Grout With Chemicals

Figure 1 illustrates in a bar chart form the overall permeability changes of acrylate grout with ten selected chemicals. On the left vertical axis of the chart permeability is plotted on a log scale. Along the horizontal axis the chart is subdivided into ten boxes, each representing one of the ten chemicals. On the right vertical axis the equilibrium permeabilities of the acrylate grout samples with water are indicated. Each shaded bar represents the average changes in the permeability of the grout with one of the chemicals. Each bar starts at the equilibrium permeability of the grout with water, and may go up or down, or remain unchanged, depending on the reaction of the grout with the specific chemical. In most cases the bar first rises to a dashed line that represents the permeability of the grout at the first peak of its permeability with flow. The bar may rise further and terminate at a permeability level that corresponds to the final equilibrium permeability of the grout with the specific chemical. The number on each line gives the number of pore volumes of chemical which flowed through the sample before it reached the indicated equilibrium permeability.

As shown in the bar chart, the acry-

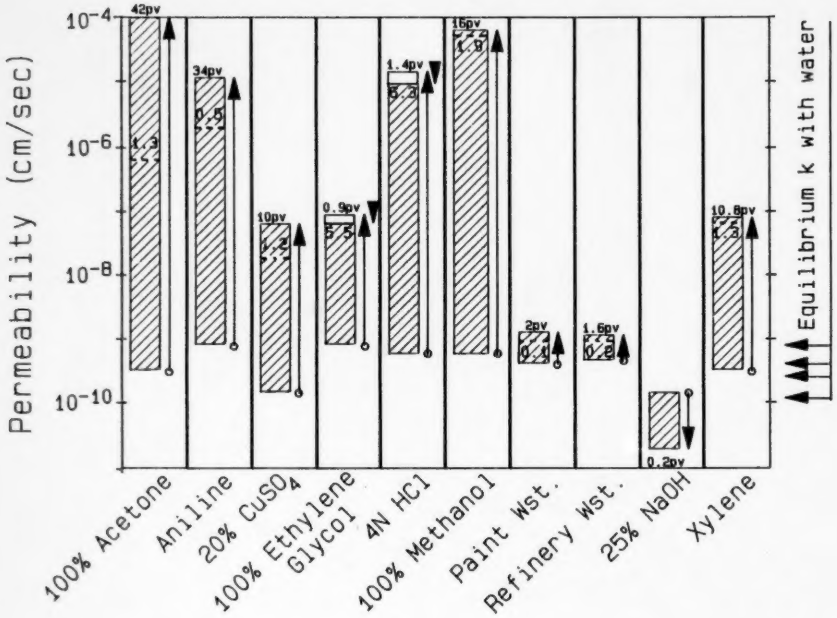

Figure 1. Permeability of acrylate grout with various chemicals.

late grout exhibited excellent resistance to real-site paint and refinery wastes, and to 25% sodium hydroxide. Its performance was satisfactory with 20% cupric sulfate, 100% ethylene glycol and xylene. The aniline, 100% acetone, 4N hydrochloric acid, and 100% methanol were very detrimental to the permeability of this grout. The permeability of the grout decreased with the introduction of 25% sodium hydroxide, however, since the flow volume was only 0.2 pore volume, this trend may reverse itself with continued flow, but only after a very long testing time.

The effects of chemical concentration on acrylate grout can be observed in Figure 2. The figure shows pairs of bars side by side, allowing the comparison of the effects of concentration of selected chemicals on the permeability of the grout. In the cases of acetone and methanol the effects of the higher chemical concentrations are very pronounced. On the other hand, the ultimate permeability of the grout was the same with both concentrations of cupric sulfate, and again with both concentrations of hydrochloric acid.

Permeability Test Results For Cement-Bentonite (Mix 2) Grout With Chemicals

The way the cement-bentonite (mix 2) grout behaved with the various chemicals is summarized in the bar chart shown in Figure 3. With both water and chemicals, this grout was the most impervious of all tested. The introduction of every chemical caused the permeability of the grout samples to decrease from their baseline permeabilities with water. With very small amounts of flow of between 0.1 and 0.6 pore volumes, the permeabilities of the samples dropped to between 3 x 10^{-11} and 6 x 10^{-11} cm/sec, or to a practically impervious state. Because of their very low permeability, these samples allowed very low flow volumes, even though they were tested on the average for more than 120 days. It is possible that given enough time and flow these chemicals could increase the permeability of this grout, but it would take very long testing times.

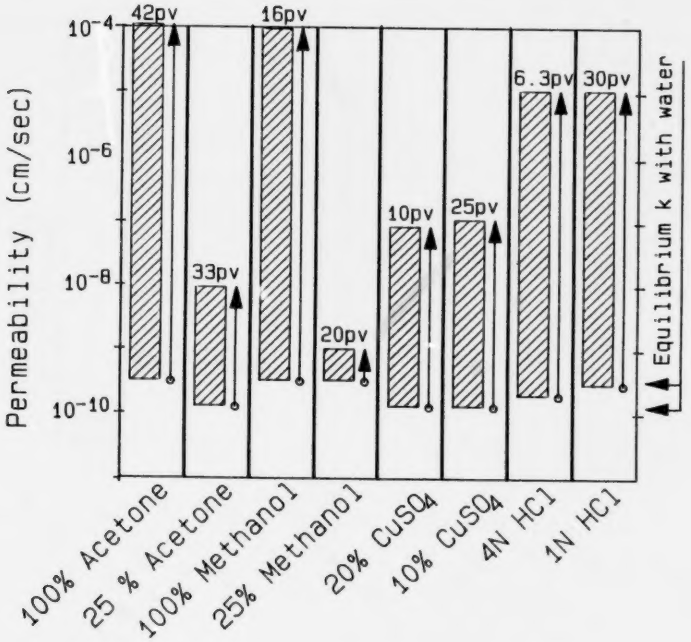

Figure 2. Effect of leachate concentration on the permeability of acrylate grout.

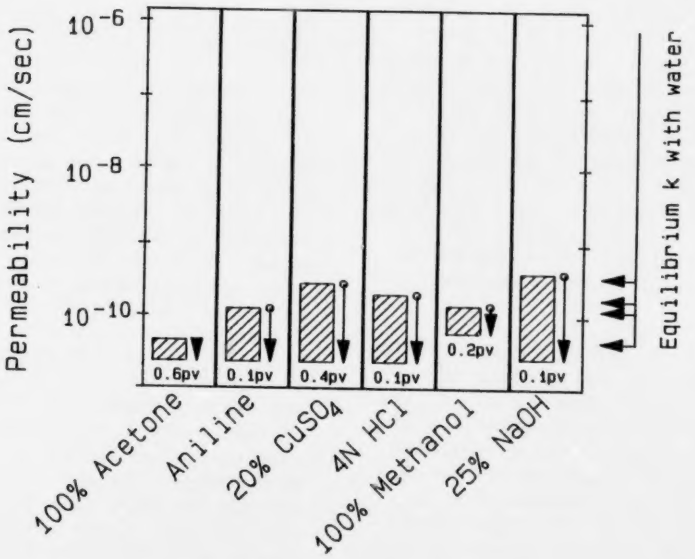

Figure 3. Permeability of cement-bentonite (mix 2) grout with various chemicals.

Permeability Test Results For Urethane Grout With Chemicals

Figure 4 illustrates in a bar chart form the overall changes in permeability of urethane grout with ten selected chemicals. As shown, the urethane grout remained quite impervious with the majority of the chemicals. With 20% cupric sulfate and 4N hydrochloric acid the grout performed marginally, as its final permeability slightly exceeded the 1 x 10^{-7} cm/sec level. The most detrimental to the urethane grout were the 25% sodium hydroxide and xylene. The sodium hydroxide caused a 4.5 orders of magnitude increase, raising the equilibrium permeability of the grout to much above the 1 x 10^{-7} cm/sec level.

The bar chart in Figure 5 shows the effects of concentration of selected chemicals on the final permeability of the urethane grout. As shown, varying the concentrations can have varying effects. For example, with 25% ethylene glycol the urethane grout samples did not exhibit increases in their permeabilities, while the samples with a 100% solution of ethylene glycol did.

Permeability Test Results For Other Grouts With Chemicals

In addition to the above discussed grouts, cement-bentonite (mix 1), sodium silicate, glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate grouts were also tested. However, the baseline permeabilities of these grouts with water ranged between 1.7 x 10^{-5} and 3.0 x 10^{-6} cm/sec, too high for cutoff construction. Nevertheless, the grouts were subjected to limited testing with chemicals and showed relatively small changes in their permeabilities.

Reactivity Tests

The objectives of the reactivity tests were to observe the weight and volume changes that small samples of the various grouts underwent during their immersion in selected chemical baths, and to explore if these observations could be correlated with the corresponding permeability test results.

In this research the three grouts tested for their reactivity were acrylate,

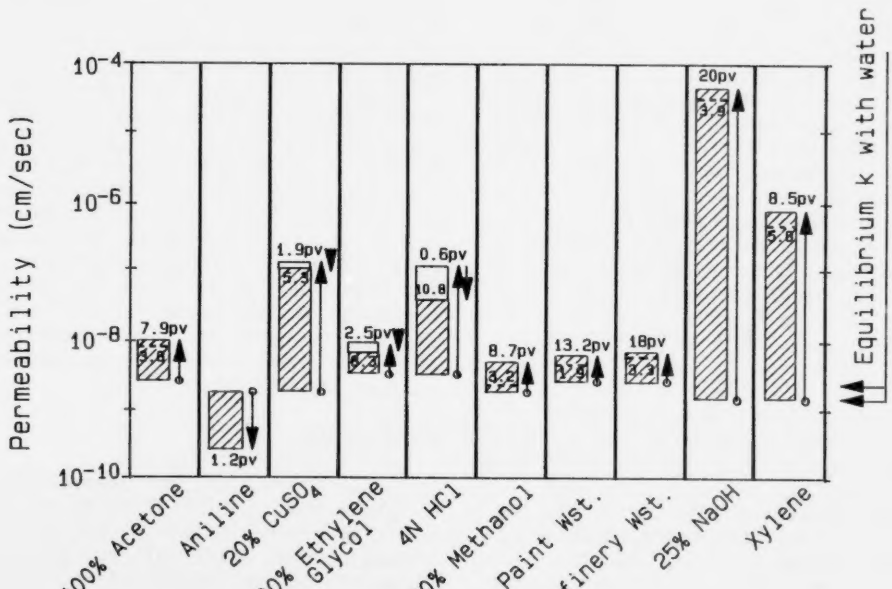

Figure 4. Permeability of urethane grout with various chemicals.

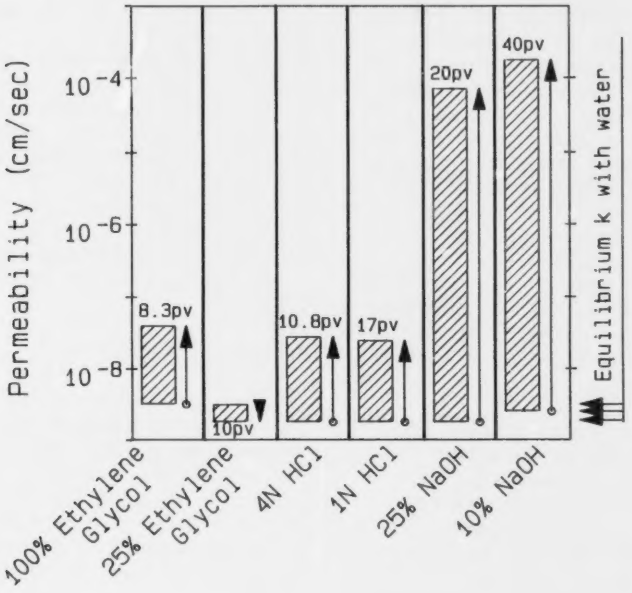

Figure 5. Effect of leachate concentration on the permeability of urethane grout.

cement-bentonite, and urethane. The testing consisted of immersing the grout samples in selected chemicals and weighing them after elapsed times of 1, 7, 14, 28, 56, and 84 days. Plots of percent weight change versus time were prepared for each sample and replicate series. In addition, subjective observations were made and recorded on the shrinkage, swelling, spalling, hardening, softening and stickiness of the samples. The results ranged from total disintegration to as much as a 40% weight increase.

COMPARATIVE ANALYSIS OF PERMEABILITY AND REACTIVITY TESTS

The results from the two types of tests were analyzed, compared, and a scheme was proposed to allow the prediction of the permeability behavior of grouts with various chemicals from their behavior with the same chemicals in the reactivity tests. This scheme is summarized in Table 1. In this table, weight and volume changes in the vertical columns, and consistency changes in the horizontal rows are correlated with permeability changes indicated in the boxes. For example the urethane samples in a xylene bath underwent medium (10%, authors' classification) weight losses, and they also became hard. This case corresponds to the matrix location column 2 and row 2, which reads: "Permeability increases significantly." Indeed, going back to Figure 4, it is seen that the permeability of the urethane grout with xylene increased almost three orders of magnitude before it came to an equilibrium. It is proposed that with the presented correlations the choice of the most suitable grout for a site could possibly be made based on reactivity tests only, and these could be conducted at the site of the hazardous waste.

CONCLUSIONS

1. When tested for permeability, the acrylate grout exhibited excellent to satisfactory resistance to all chemicals, except reagent grade aniline, 100% acetone, 1N and 4N concentrations of hydrochloric acid, and 100% methanol. These caused increases of several orders of magnitude in its permeability.

TABLE 1. PREDICTED PERMEABILITY BEHAVIOR BASED ON REACTIVITY TEST RESULTS

WEIGHT/ VOLUME CHANGES / CONSISTENCY CHANGES	VOLUME INCREASE/ WEIGHT GAIN	VOLUME DECREASE/ WEIGHT LOSS	WEIGHT LOSS BY SPALLING	INITIAL VOLUME INCREASE, LATER SHRINKAGE (INITIAL WEIGHT) GAIN, WEIGHT LOSS AS TEST PROCEEDS)	INITIAL VOLUME DECREASE, LATER VOLUME INCREASE (INITIAL WEIGHT LOSS, WEIGHT GAIN AS TEST PROCEEDS)
None			Moderate increase in permeability		
Remains hard or becomes hard		Permeability increases significantly		Considerable increase in permeability	Large increase in permeability
Softens	Permeability decreases somewhat, or at worst, increases minimally			Permeability affected minimally	
Softens quickly		Increase in permeability is small			Moderate increase in permeability
Softens slowly		Increase in permeability is large			
Disintegrates	Permeability increases greatly				

2. With all the chemicals tested, the permeability of the cement-bentonite (mix 2) grout decreased from its baseline permeability with water to a practically impervious permeability of approximately 3×10^{-11} cm/sec.

3. The urethane grout remained quite impervious with the majority of the chemicals tested, except it performed only marginally with 20% solution of cupric sulfate, and 1N and 4N concentrations of hydrochloric acid, and poorly with 25% solution of sodium hydroxide and reagent grade xylene.

4. The effects of the concentration of chemicals on the permeability of grouts varied. It was found from the limited data that some chemicals with reduced concentrations caused smaller increases in the permeability of a grout than with higher concentrations, while with other chemicals, varying the concentration had no significant effect.

5. From the analysis of reactivity and permeability test results, a scheme was proposed that correlates the weight and consistency changes of the reactivity samples of a grout immersed in a chemical, to expected changes in its permeability when permeated by the same chemical. This may allow an engineer to make at least the preliminary selection of suitable grouts for a site by using reactivity tests in place of the more costly permeability tests.

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ELECTRO-DECONTAMINATION OF CHROME-CONTAMINATED SOILS

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ABSTRACT

A technique of in-situ treatment of inorganic waste-contamined soils is being explored at a Superfund site in a current study. Transport of inorganic ions under an imposed electric field is essentially the basis of this technique. In this paper, the results of the laboratory experiments conducted on undisturbed soil samples obtained from the site and the initial results of preliminary field experiments are reported.

Generally, the laboratory results have shown that with appropriate combination of applied hydraulic and electric fields, it is possible to remove chromium at a faster rate by this approach than by hydraulic leaching alone. The preliminary field experiments also show that chromium concentrations can be altered by electro-kinetic treatment alone.

INTRODUCTION

In the past, electro-kinetics have been applied in a variety of engineering projects. Mostly, these applications made use of the electro-osmotic transport of the liquid phase. The past applications include dewatering and consolidation of soils (3,5), recovery of embedded objects from the ocean floor (4), alteration of penetration or pull-out resistance of piles (2), dewatering of sewage sludge (8), and mine tailings ponds (9) and dredge spoils (11), and increasing recovery rates in oil fields (1) among others. Some previous studies have also indicated that, from a technical point of view, electro-kinetic treatment of the ground may be a feasible approach for decontaminating waste-contaminated soils (6,7,10).

However, the practical effectiveness and feasibility of such a technique have not been explored. Definitive field-scale testing is required prior to widespread application of the technique. This project was, therefore, undertaken as a field-scale study, the scope of which included a) characterization of the soil-water electrolyte system at a Superfund site in Corvallis, Oregon, b) bench-scale studies and design of in-situ electro-kinetic experiments, c) performance of a series of field tests and d) establishment of some possible relationships between the extent (and rate) of decontamination and the important experimental variables based on the field test results. The project is only partially complete at present. The underlying concepts of the treatment and some of the up to date findings are reported in this paper.

APPROACH

The processes associated with the flow of direct-current electricity through soil-water electrolyte systems are collectively termed electro-kinetics. These include electro-osmosis, electrophoresis, and other electro-chemical processes. These processes mainly cause relative movement of electricity (current flow), ions (ionic drift), charged particles (electrophoresis) and of the liquid phase (electro-osmosis). The major effects of electro-kinetic processes are movement of water, ionic drift, ion exchange, development of osmotic and pH gradients, electrolysis, hydrolysis, oxidation, reduction, heat generation, gas evolution, formation of secondary minerals, physical and chemical adsorption, and many others. The overall effect is quite complex and the present-day understanding is not up to the task of quantitatively accounting for all of these effects of electro-kinetic processes. Nevertheless, the empirical evidence from the past applications leads one to believe that electro-kinetics may have some possible applications in waste-management. A partial list of the potential applications of electro-kinetics in waste management is shown in Table 1. The present project attempts to evaluate the practical effectiveness of electro-kinetics as the primary method of treating waste-contaminated soils.

TABLE 1

APPLICATIONS OF ELECTRO-KINETICS IN WASTE MANAGEMENT

-- AS PRIMARY METHOD OF TREATMENT

Water-borne and adsorbed offensive elements can be made to flow toward wells (electrodes) and can be extracted from the ground.

-- AS AID TO OTHER ALTERNATIVE TECHNIQUES

a) With Excavation of Contaminated Soil

Soils which are difficult to dewater by conventional techniques can be dewatered; need to excavate may be eliminated by lowering the water table.

b) With Installation of Impervious Barriers

For grout curtains, sheet piles and floor seals, etc., electro-kinetics can be used to enhance placement at desired locations and thereby remove uncertainties in forming an impervious seal.

c) With Injection of Chemical or Biological Detoxifying Agents

Electro-kinetics can be used to assure uniform distribution and improve effectiveness.

d) With Collection of Contaminant Plumes by Pumping

Electro-kinetics can be used to reduce dilution by surrounding fresh water. Contaminant plumes may be directed back to waste site for containment or treatment.

BACKGROUND

Site History

The field evaluation of electro-kinetic treatment is being conducted in Corvallis, Oregon within the confines of an abandoned industrial hard chrome plating facility, previously called United Chrome Products, Inc. (UCPI). The site is one of the nation's Superfund sites and is situated next to the Corvallis Airport, south of the Airport Road. The UCPI facility and its immediate vicinity is shown in the site location plan (Fig. 1). UCPI conducted a chromium plating operation at the site from 1956 to 1985 and is reportedly responsible for discharging liquid plating wastes into the subsurface soils at the site. The principal locations of discharge were the dry well disposal pit on the west end of the building and some leaky plating tanks inside the building.

Subsurface Conditions

The project site is located on the alluvial plains of the Willamette River Valley and occupies about 1.5 acres of level ground. Detailed investigation of the conditions at the site was carried out by the CH$_2$M Hill Company under a contract with the USEPA Hazardous Waste Site Control Division of the Region 10 office and is available in the report for Contract No. 68-01-6692. This report reveals that the subsoils are characterized generally by unconsolidated deposits of clay, silt and gravel which can be broken into three distinct units, an upper aquifer, a lower aquifer and an aquitard separating the two aquifers. The upper soils in the profile consist of about 2 to 3 ft. of miscellaneous fill or top soil and 15 to 20 ft. of clayey silt to silt ranging from mottled grayish brown to bright yellow in color. This layer of soil extends to a depth of 17 to 21 ft. below the ground surface. The less pervious soil layer which separates the two saturated previous zones, consists of light blue to dark gray clay to silty/sandy clay ranging in thickness from 2.5 to 12 ft. The bottom of this layer extends from 22 to 29 ft. in depth below the ground surface over the site. The lower aquifer consists of wet, fine to coarse sands and gravels and is at least 15 ft. thick at the site. The

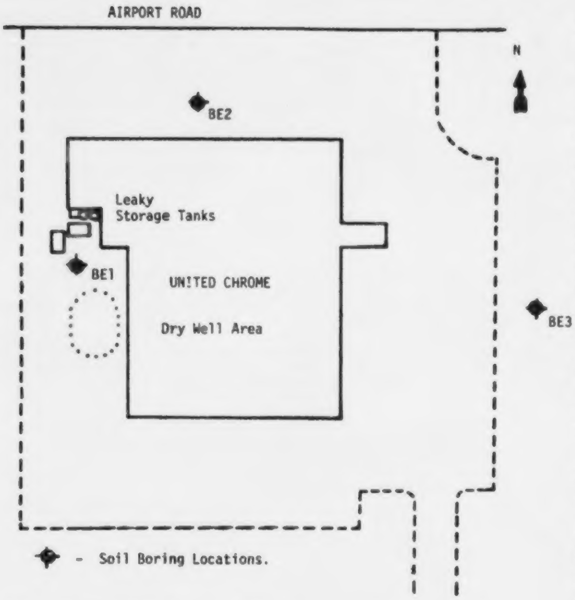

Fig. 1: Location plan for soil borings.

groundwater table fluctuates seasonally between 0 to 10 ft. below the ground surface and has a slope of approximately 5 ft. per mile in the north-northeast direction.

Site Characteristics

The near-surface soils are heavily contaminated with chromium and the distribution of the contaminant concentration is greatly variable (100 - 10000 mg/l) with depth and distance from the source points. Fortunately, the affected soils have low permeability (ranging from 5 x 10^{-4} cm/sec. to 5 x 10^{-6} cm/sec.) and there is very little flow of groundwater at the site, the average hydraulic gradient at the site being only 0.008 ft./ft. In fact, the risk of proliferation is increased by the presence of the open ditch which runs along the northern edge of the site. During the winter the standing water in the ditch comes in direct contact with the groundwater and carries contaminants up to the Willamette River.

The general characteristics of the site were assessed in view of the potential application of electro-kinetic treatment. These characteristics, e.g. moderately large areal extent of the site, nearly static groundwater regime and saturated moderately permeable soils at shallow depth and relatively simple chemistry of the wastes, are ideally suitable for in-situ electro-kinetic treatment. The size of the site is neither so large that an untested technique might be considered too risky for the benefits expected, nor it is so small that excavation and disposal at a secure facility can be considered desirable. Again, the near-surface contaminated soils which range from clayey silts to silty clays are not permeable enough to be easily treated by in-situ leaching. The major ionic constitutents of the contaminants at the site are trivalent and hexavalent chromium (Cr III cationic form, and Cr VI anionic form). The anionic chromium, being more stable in the pH range of the groundwater at this site, is more predominant in the soil-water system. Hexavalent chromium is relatively unreactive with soil and is not expected to be significantly retarded in its migration by adsorption or precipitation. Furthermore, the high enough concentration and ionic mobility of chromium are also favorable factors. Hence, it seems quite likely that it can be transported with the induced flow with relatively high efficiency and with low electrical power consumption.

PRELIMINARY RESULTS AND DISCUSSION

Laboratory Tests

To aid in the design and development of a field test program, a field exploration effort was first devoted to obtaining representative samples of contaminated on-site soils. These samples were brought back to the laboratory to evaluate the pertinent geotechnical and chemical characteristics of the soil and pore water and to develop some bench-scale data on the effects of electro-kinetic treatment.

The laboratory tests were carried out in a specially designed electro-kinetic cell. It was decided that combining of hydraulic leaching with electro-kinetic treatment may be appropriate, since maintaining continuous flow of liquid across the sample would eliminate desaturation due to trapping of evolved gases in the sample. The effectiveness of electro-kinetic treatment was observed by comparing the results of hydraulic leaching experiments with those of combined hydraulic and electro-kinetic experiments.

Chromium removal by leaching of the soil column appeared to depend only on the total water flow through the sample and was apparently independent of the hydraulic gradient (or pressure difference) across the sample. Results from the tests are presented as normalized plots of cumulative fraction of chromium removed against cumulative volume of water leached per unit volume of soil sample. Fig. 2 shows that no significant difference in the total fraction of chromium removed was noticeable even though Experiments 1 and 2 were carried out at variable pressure differences across the sample. These results indicate that in the case of hydraulic leaching alone the principal mechanism of chromium removal is miscible displacement. The results of Experiments 1 and 2 were used as a comparison basis for the electro-kinetic effect on chromium removal in the subsequent experiments.

In the later experiments, DC electric fields were applied across the sample in addition to the hydraulic leaching. The first few experiments which combined hydraulic leaching and electro-kinetic treatment were carried out with frequent reversal of the direction of fluid flow or electric field. The superposition of electric field was seen to either reduce or enhance removal rate depending upon the point of collection of net hydraulic flow or effluent. While anodic effluent showed an increase in the rate of removal, cathodic effluents showed a decrease. In Experiments 5, 7, and 8, the effluents were collected at the anode. Fig. 3 shows a comparison of the results of Experiment 1 (and 2 combined) with those of Experiments 5 and 7 carried out at different field strengths. It can be seen from Fig. 3 that in order to achieve 95% removal of chromium, Experiments 1 (and 2 combined), 7 and 5 would require passing of net fluid flow of 1.1., 0.8, and 0.5 times the volume of soil treated. In other words, electro-kinetics may significantly decrease not only the time of in-situ treatment, but also the amount of leachate water to be treated elsewhere.

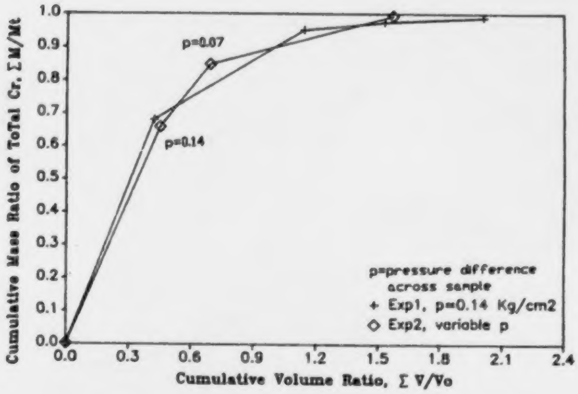

Fig. 2: Effect of hydraulic gradient On Cr removal by leaching.

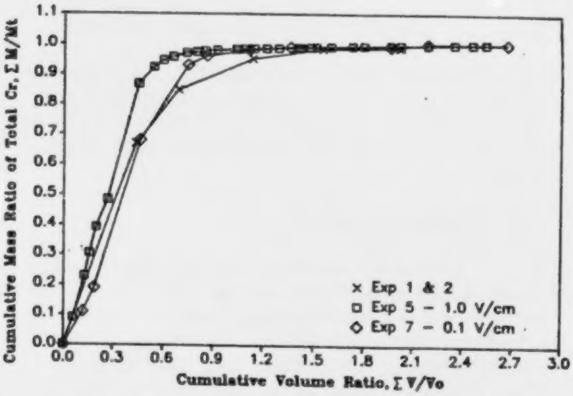

Fig. 3: Comparison of effects of combined treatment and hydraulic leaching.

Field Test Program

Although the laboratory test results indicate that simultaneous application of hydraulic and electrical gradients in opposite directions is necessary for removal of (anionic) chromium, this may be an artifact of the laboratory electrokinetic cell. In order to prevent desaturation of the laboratory sample near the anode, it was necessary to maintain flow through the sample by hydraulic leaching. For field soils, this may not be warranted and it may be possible to subject the field soils to electrokinetics alone for treatment. Hence, it was considered appropriate to adopt a two-stage approach for field activities in order that such uncertainties can be resolved. The field-scale effort was split into: a) feasibility-level experiments and b) final experiments. The purpose of the feasibility level experiments was evaluation (if possible) of the effectiveness of the process of ionic migration, identification and elimination of possible experimental difficulties, calibration of instrumentation and estimation of hydraulic and electro-kinetic conductivity parameters in the field. The major emphasis was to check in the field whether anionic chromium can be mobilized towards the anodes simply due to the process of ionic migration under electrical field or if migration of chromium ions takes place in the direction of movement of the bulk solution.

The field-scale operations were designed in as much detail as possible by giving proper consideration to: a) electrode configuration and material, b) hydraulic leaching system, c) monitoring system and d) power source and consumption. The shallow well BE1 shown in Fig. 1 was chosen to serve as the cathode. The anodes were installed at the vertices of a regular hexagon (5 ft. spacing) with the cathode being at the center of the hexagon. The anodes were reinforcing steel rods (0.25 in. diameter, 20 ft.long) inserted in 15 ft. deep slotted PVC tube wells. An alternate set of four such anodes was also placed in a square pattern (8 ft. spacing) around the cathode. During the experiments, the response of the soil-water electrolyte to the treatment was designed to be monitored and controlled by keeping measurement records of the important experimental variables, e.g. applied potential, total current flow across the pairs of electrodes, pH, con-

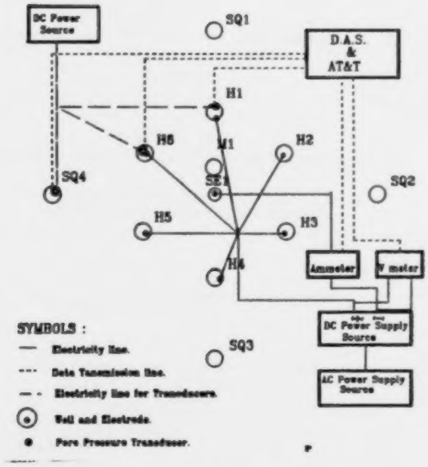
DC Power Source
SQ1
D.A.S. & AT&T
H1
H6
M1
H2
SQ4
SE1
SQ2
H5
H3
H4
Ammeter
V meter
DC Power Supply Source
SYMBOLS :
Electricity line.
Data Transmission line.
Electricity line for Transducers.
Well and Electrode.
Pore Pressure Transducer.
SQ3
AC Power Supply Source

Fig. 4: Schematic plan for field experimental setup.

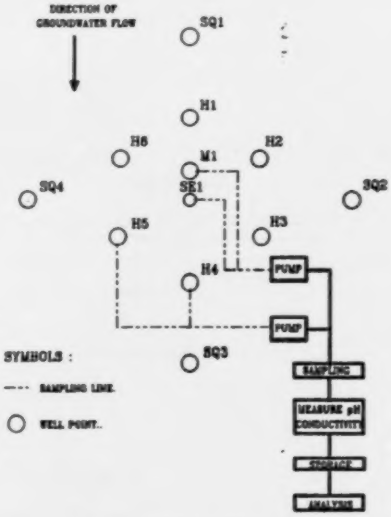
DIRECTION OF GROUNDWATER FLOW
SQ1
H1
H6
H2
M1
SQ4
SE1
SQ2
H5
H3
H4
PUMP
PUMP
SYMBOLS :
SAMPLING LINE.
WELL POINT.
SQ3
SAMPLING
MEASURE pH CONDUCTIVITY
STORAGE
ANALYSIS

Fig. 5: Schematic plan for monitoring and sampling system.

ductivity, chromium concentration, temperature, redox potential of the effluent, time of sampling and length of treatment time, hydraulic flow volume injected or withdrawn and levels of standing water in the wells. A schematic plan of the electrodes and the electrical connections for the field set up is shown in Fig. 4. Fig. 5 shows the schematic plan of the monitoring and sampling system.

Three preliminary sets of experiments with hexagonal and square anode geometry have been completed. The early indications are very promising. The typical results obtained from the first two consecutive experiments are shown in Figs. 6 and 7.

The first test was carried out for 26.5 hours with 5-volt potential difference across the anodes arranged in the hexagonal pattern and the cathode. The second test was performed by applying 30 volts across the same electrodes for 5 hours. Figs. 6a) and 7a) show temporal variations of pH values of the water samples extracted from the cathode (SE1), one of the anodes (H5) and the intermediate monitoring well (M1). The temporal variations of concentration of chromium in those samples are shown in Figs. 6b) and 7b). It can be noted that pH values are increasing at SE1 and M1 and decreasing at H5. This is expectedly due to electrolysis of water at and near the cathode and dissolution of ion at the anode. Unfortunately, the trend in the variation of chromium concentration is apparently confusing. The decrease in concentration of chromium at the anode is unexpected. This anomolous change at the anode may have been caused by coprecipitation of chromium with iron oxide produced by anodic dissolution. The decrease of chromium concentration at the

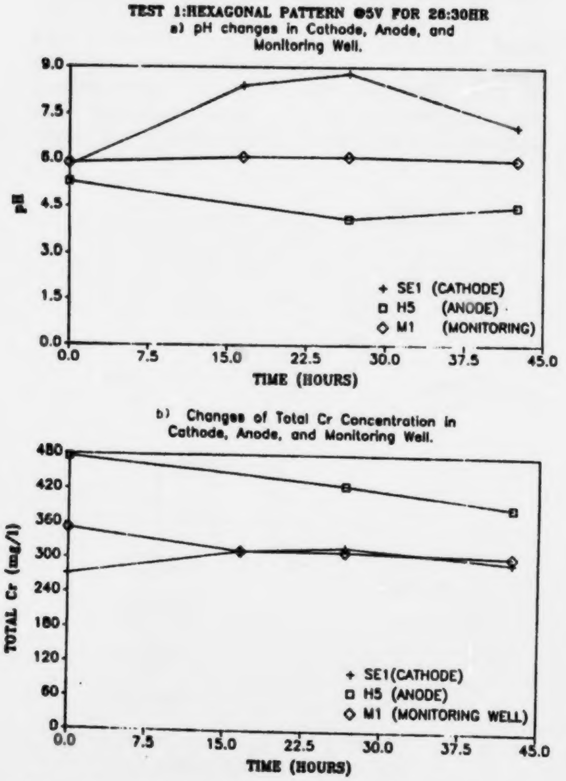

Fig. 6: Temporal variations of pH and Cr concentration during Test 1.

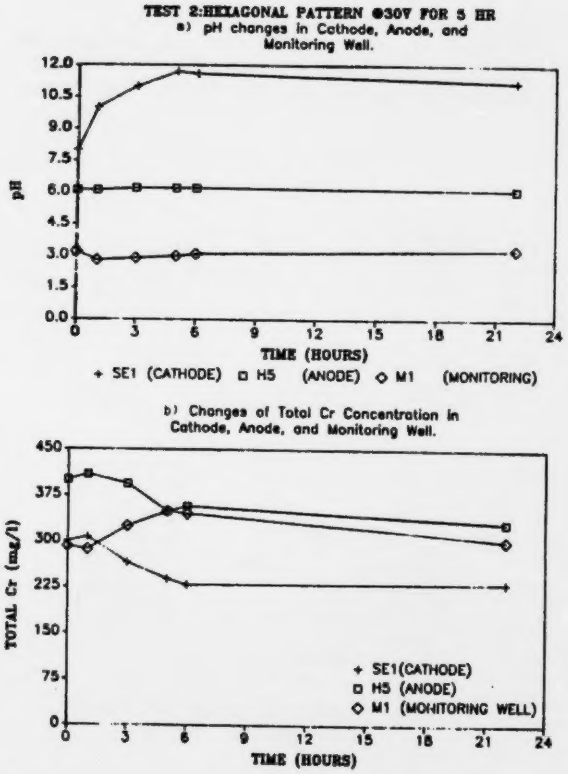

Fig. 7: Temporal variations of pH and Cr concentration during Test 2.

cathode with simultaneous increase at the monitoring well may be indicative of ionic transport due to electrical treatment during the second test. Further assessment of the preliminary test data is continuing and a more coherent understanding of the process may emerge in the near future.

CONCLUSIONS

The following conclusions may be drawn from the results of the experiments conducted so far:

(1) Laboratory tests have shown that a combination of electro-kinetic and hydraulic treatment can accelerate the process of chromium removal substantially compared to hydraulic treatment by itself. This acceleration should be much more pronounced in the field operations where the hydraulic gradient which can be practically applied (and consequently the flow) will be very small.

(2) The possible mechanisms involved in the treatment are dispersion due to hydraulic flow, ion migration, electrolysis of water, adsorption/desorption and chromium reduction due to imposed electric field. There are significant experimental and theoretical problems in quantitatively assessing these factors and their interactions.

(3) Considerable work is still needed to reach general guidelines for use of this technology. Continued laboratory experimentation is needed to accompany field studies and laboratory studies should evolve to extend the range of physical and chemical conditions studied.

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CURRENT STATUS OF THE DESIGNATION AND ADJUSTMENT OF CERCLA HAZARDOUS SUBSTANCES AND THEIR ASSOCIATED REPORTABLE QUANTITIES

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ABSTRACT

In this paper the U.S. Environmental Protection Agency (EPA) describes the technical methodology it has used to adjust reportable quantities (RQs) of CERCLA hazardous substances, which when released into the environment must be reported to the National Response Center (NRC), and the methodologies the Agency is considering for designation of additional CERCLA hazardous substances. In accordance with CERCLA Section 102, the EPA Administrator may promulgate regulations to establish the level of release of a hazardous substance which must be reported to the NRC. The methodology considers the intrinsic physical/chemical, toxicologic, and degradative properties of the hazardous substance. The Administrator issued Final Rules on April 4, 1985 and on September 29, 1986 which adjusted the statutory RQs of 442 of the 717 CERCLA hazardous substances. Section 102(a) of CERCLA provides the Administrator with the authority to designate additional hazardous substances and adjust their RQs. The options available to the Administrator for choosing those substances most appropriate for designation are also described.

INTRODUCTION

This paper is a status report of the U.S. Environmental Protection Agency's (EPA's/Agency's) progress to date on the adjustment of the statutory Reportable Quantities (RQs) of the hazardous substances (HS) as defined in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund"), and on the Agency's strategy for designating additional CERCLA HS as provided for in CERCLA Section 102(a). It also discusses the status of other EPA regulations related to the reporting of releases of HS and other potentially harmful chemicals.

This paper is relevant to this conference on hazardous waste research because the reporting provisions of CERCLA and its implementing regulations are not limited to episodic releases such as those which sometimes occur during transportation incidents, for example, but apply to any release which reaches the environment such as those which occur at hazardous waste sites.

BACKGROUND

The CERCLA Hazardous Substances

The term "hazardous substance" has a very specific meaning according to CERCLA.

Section 101(14) of CERCLA defines a hazardous substance as:

1. Any substance designated pursuant to Section 311(b) of the Clean Water Act (CWA);
2. Any hazardous waste having characteristics identified under or listed pursuant to Section 3001 of the Solid Waste Disposal Act, otherwise known as the Resource Conservation and Recovery Act (RCRA);
3. Any toxic pollutant listed under Section 307(a) of the CWA;
4. Any hazardous air pollutant listed under Section 112 of the Clean Air Act (CAA);
5. Any imminently hazardous chemical substance or mixture with respect to which the Administrator of EPA has taken action pursuant to Section 7 of the Toxic Substances Control Act (TSCA); and
6. Any element, compound, mixture, solution or substance the Administrator determines to be hazardous pursuant to Section 102 of CERCLA.

There are currently 717 HS composed of 611 unique chemical compounds and 106 waste streams. This total does not include chemicals or mixtures that exhibit characteristics of ignitibility, corrosivity, reactivity, or extraction procedure toxicity according to 40 CFR 261.20. Such chemicals and mixtures are also considered HS, but because it would be impossible to identify all such chemicals and mixtures, they are not specifically listed under RCRA, and therefore, they are not specifically listed under CERCLA. As of this date the Administrator has not exercised his authority to designate any new substances as CERCLA HS pursuant to Section 102.

Notification Requirements

Section 103(a) of CERCLA requires any person in charge of an offshore or onshore facility or a vessel to report to the National Response Center (NRC) as soon as that person has knowledge of any release of a HS that is equal to or greater than the RQ for that HS. The term "facility" includes active and inactive hazardous waste sites. Once the NRC is notified, it informs the predesignated On-Scene Coordinator (OSC) pursuant to the National Contingency Plan (40 CFR 300) of the release. The OSC evaluates the circumstances of the release, gives the pertinent information to appropriate state and local officials and decides whether, and in what manner the Federal government should respond to the release.

Adjustment of Reportable Quantities

Congress assigned statutory RQs to the HS in Section 102(b) of CERCLA. All of the HS received statutory RQs of 1-pound except those HS that were designated pursuant to Section 311(b) of the CWA which received statutory RQs equal to the RQs assigned pursuant to Section 311(b)(4) of the CWA and codified in 40 CFR 117. Section 102 of CERCLA also authorizes the Administrator to adjust the statutory RQs of the HS.

Rulemaking History

Adjustments to Statutory RQs. The Agency has promulgated final adjusted RQs for 442 HS in two separate rulemaking actions. The first of these final rules was published in the Federal Register on April 4, 1985 (50 FR 13456 - 13513). It finalized adjusted RQs for 340 HS. The other final rule was published on September 29, 1986 (51 FR 34534 - 34549) and it finalized adjusted RQs for 102 HS. Most of these 102 HS had been identified as chronic toxicants. On March 16, 1987 the Agency published a Notice of Proposed Rulemaking (NPRM) (52 FR 8140 - 8171) that proposed adjustments to an additional 273 of the remaining 275 HS. This proposed rule presents the Agency's methodology for adjusting statutory RQs on the basis of potential carcinogenicity. The two remaining HS, lead and methyl isocyanate, are still being studied by the Agency, and may have their statutory 1-pound RQs adjusted in the future.

Also, in the Federal Register on March 16, 1986 the Agency published another NPRM that proposed adjustments to the 1-pound statutory RQ for Radionuclides (52 FR 8172 - 8186). This broad generic category includes thousands of separate substances, and therefore neither the category nor the individual radionuclides are counted among the 717 CERCLA HS.

Designation of Additional Hazardous Substances. The Agency has solicited comments on various methods that could be used to designate additional HS in an Advance Notice of Proposed Rulemaking (ANPRM) published in the Federal Register on May 25, 1983 (48 FR 23602 - 23605).

The Reauthorized Superfund

On October 17, 1986 the President signed the Superfund Amendments and Reauthorization Act of 1986 (SARA). The SARA is a law that strengthens the EPA's role in state environmental activities, increases the liability of private companies, and imposes strict requirements on settlement provisions, judicial review, and cleanup standards. In the reauthorized CERCLA, Congress included Title III (The Emergency Planning and Community Right-to-Know Act of 1986) which was designed to prevent a catastrophe similar to the incident which occurred in Bhopal, India in 1984 with the release of methyl isocyanate.

Title III provides for the establishment of emergency plans at the local level based on data from facilities in the area. Chemicals stored at these facilities are reported to a Local Emergency Planning Committee (LEPC), which then will consider how to handle a situation in the event of a release of that chemical. In order to implement the system, Congress has defined the chemicals and their quantities that shall be subject to this reporting requirement. The Title also provides for civil and criminal penalties for failure to comply.

RQ ADJUSTMENT

A previous paper (1) provided a detailed description of the methodology the Agency uses to adjust the statutory RQs of the CERCLA HS. In addition, the reader is referred to the Technical Background Documents that provide the technical basis for the RQ adjustment methodology (2)(3)(4). The following is a brief description of the RQ adjustment methodology.

The RQ adjustment methodology consists of two major steps. The first major step involves evaluation of the physical, chemical and toxicological characteristics of each HS. The primary criteria examined are: aquatic toxicity, acute mammalian toxicity (oral, dermal, and inhalation), ignitibility, reactivity, chronic toxicity, and potential carcinogenicity. For each primary criterion a five-tier rating scale is used, corresponding with RQ values of 1, 10, 100, 1000, and 5000 pounds. Since this five-tier system was successfully used in the CWA and both the regulated community and response personnel are familiar with it, the Agency has decided to use this methodology for adjusting the statutory RQs of the CERCLA HS.

The Agency has proposed to use only three of the five RQ levels (1, 10, and 100 pounds) for assigning adjusted RQs to the CERCLA HS that are potential carcinogens. This decision is based on the special properties associated with potential carcinogens and an analysis of the risks posed by their release. A complete discussion is provided in (4).

Each HS is evaluated according to the primary criteria and an RQ value is determined for each applicable criterion. The primary criteria RQ for each HS is the lowest value of all the applicable criteria. For example, if a particular HS's ignitibility corresponds to a RQ of 1000 pounds, chronic toxicity to a 5000 pound RQ, aquatic toxicity to a 10 pound RQ, mammalian toxicity to a 100 pound RQ, and reactivity to a 1000 pound RQ, the primary criteria RQ is 10 pounds, based on the RQ for aquatic toxicity. The Agency then evaluates each HS according to a set of secondary criteria consisting of biodegradation, hydrolysis, or photolysis (BHP). The primary criteria RQ is then raised one level if an analysis indicates that the HS naturally degrades by BHP into less hazardous products when released into the environment.

Research Needs

The Agency recognizes that technical updates to the final rules on RQ adjustments will be an ongoing process because; 1) the RQ adjustment methodology relies on existing data in the areas of health effects, aquatic toxicity, ignitibility, reactivity, and degradation in the environment, many of which are areas of active research, and 2) the Agency is active in the areas of generating and reviewing data on the toxicology of chemicals. Technical updates of promulgated adjusted RQs are appropriate because such updates will result in RQs that are more accurate and which will better protect the public health, welfare, and the environment, and in those cases where additional data result in raising an RQ, will lessen compliance burdens on the regulated community.

The Agency will periodically review the published and unpublished literature for the purpose of using the highest quality data for RQ adjustment purposes. When new data are found that affect the adjusted RQ of a HS the Agency will propose a new adjusted RQ in the Federal Register in a technical update rulemaking. In addition, the Agency will accept for review data on chemicals supplied by the public from the literature or from laboratory studies, and if warranted, propose adjusting the RQ of the HS in question.

An analysis of the current data set on the CERCLA HS reveals the following statistics :

1. There are 215 HS (35%) without aquatic toxicity data, although some of these are gases or are insoluble in water.
2. There are 193 HS (32%) without acute mammalian oral toxicity data, although some of these are gases.
3. There are 497 HS (81%) without acute mammalian inhalation toxicity data, although some of these are solids not normally available as dusts or low vapor-pressure liquids.
4. There are 542 HS (89%) without acute mammalian dermal toxicity data, although many of these are gases.
5. There are six HS (1%) that have adjusted RQs (either final or soon to be proposed) based on either LDlo or LClo data (the lowest dosage or concentration known to have been lethal to an individual of the test species). Such data are generally from limited studies that were unable to produce suitable LD50 or LC50 data, or from accidental poisonings (see Table 1 for definitions of LD data).
6. It is believed that the data collected on ignitibility and reactivity represent a complete data set since ignitibility is based on the fundamental physical properties of boiling point and flash point, and reactivity is based on well known polymerization and water reaction tendencies. The methods for measuring these properties were established many years ago and massive amounts of such data have been generated.

DESIGNATION OF NEW CERCLA HAZARDOUS SUBSTANCES

Section 102(a) of CERCLA provides the Administrator of EPA the authority to designate as hazardous any element, mixture, solution, or substance, which, when released into the environment, may present substantial danger to the public health or welfare or the environment. As mentioned previously, the Agency published an ANPRM on designation on May 25, 1983 (48 FR 23602 - 23605). The Agency is considering several sources of candidate substances for designation, including the lists mandated by SARA and from other sources.

Reasons for Designating Additional Hazardous Substances

The reasons for designating additional substances are:

1. The lists pursuant to CERCLA Section 101(14) are not all inclusive of potentially harmful substances.
2. Designation of substances as HS encourages greater care in handling.
3. Designation of substances as HS encourages recycling.
4. Designation of substances as HS provides the Administrator the mechanism of recovering costs for cleanup.

Each of these reasons is discussed below.

CERCLA Section 101(14) Lists Are Not All Inclusive. Many substances which are hazardous to the public do not necessarily qualify to be on the lists Congress identified in CERCLA Section 101(14). Those lists were developed to protect a single medium, or, in the case of hazardous wastes, to protect the public from improper disposal and other mishandling of hazardous wastes. Each of the lists is responsive to one or more sections of environmental statutes, i.e., the Clean Air Act, the Clean Water Act, the Solid Waste Disposal Act, and the Toxic Substances Control Act. To meet the Congressional requirements of those acts, the Agency developed technical criteria to be applied to chemicals and/or wastes. These criteria were designed to specifically meet certain requirements of the acts.

Congress anticipated that by providing a multiplicity of lists, taken from several regulations developed pursuant to the acts discussed above, most substances which provide increased risks to the public, welfare and environment would be covered. However, Congress recognized that the umbrella of these four major environmental acts might not cover all the substances from which the public should be protected (e.g., Congress did not include the Federal Insecticide, Fungicide, and Rodenticide Act [FIFRA] active ingredients). Accordingly, Congress gave the Administrator authority to designate additional substances as CERCLA HS, thus removing the media constraints from the Administrator in designating HS.

Designation Encourages Safer Handling Procedures. Experience has shown that liability for cleanup, pursuant to Section 107 of CERCLA, has made handlers of HS more cognizant of the risks HS pose to the public. Accordingly, more attention is paid to handling, packaging, shipping, storage, and general treatment of HS. Thus, there is a tendency for industry to treat designated HS in a safer manner than pollutants and contaminants.

Designation Encourages Recycling. Many chemicals produced, used, or processed by manufacturers often are discarded when they become contaminated or otherwise out of specification. Frequently, it is more economical to discard the chemical than to recycle it. Discarding, of course, does not eliminate the chemical; usually it is sent to a landfill. If the chemical is a pollutant or contaminant it may go to a sanitary landfill where it can eventually migrate to ground waters or perhaps become airborne. If that chemical does not pose a threat to the health, welfare or environment, then disposal in a landfill is both economical and safe. However, if the chemical does pose a threat, in the absence of regulation, it can still be discarded in a sanitary landfill at a relatively low cost. On the other hand, if that substance is a designated HS, disposal in a sanitary landfill is not acceptable, and the cost of disposal in a suitable landfill is high. In most cases the cost of disposal can exceed the cost of recycling. Hence, in order to encourage industry to both conserve resources and to protect the public health, welfare and the environment, substances which do pose threats should be designated as HS to reduce the total quantity of those undesignated but harmful substances in waste disposal sites.

Designation Provides the Administrator the Mechanism for Recovering Costs of Cleanup. Section 106 of CERCLA provides the EPA with a mechanism to recover government costs for cleanup of spills of HS from owners or operators, or from other responsible parties. CERCLA does not provide a mechanism for cost recovery if the substance for which remedial action was taken is not a CERCLA HS. Furthermore, owners or operators can be liable for up to $50 million for damage to the environment caused by releases of HS. No such liability exists for damage due to releases of non-CERCLA HS. Therefore, in order to protect the SUPERFUND and to correct environmental damages, it is incumbent on the Administrator to designate as HS those substances which when released into the environment are likely to trigger a government response.

Candidate Substances for Designation from SARA

Both Title III of SARA (Emergency Planning and Community Right-to-Know Act) and Title I of SARA (Provisions Relating Primarily to Response and Liability) provide source lists the Agency is considering for designation purposes.

The Extremely Hazardous Substances. Section 302 defines the specific list of Extremely Hazardous Substances (EHS) and requires the Agency to publish the list within 30 days after the enactment of SARA. The list of EHS is defined as "the list of substances published in November, 1985 by the Administrator in Appendix A of the Chemical Emergency Preparedness Program Interim Guidance." This list was established by the Agency to identify chemical substances which could cause irreversible health effects from accidental releases. Any facility making, using or storing EHS above a promulgated threshold planning quantity must report the quantity to the Local Emergency Planning Committee (LEPC). Furthermore, a release of an EHS must be reported to the LEPC if the release is in a quantity at or above the promulgated release notification quantity. If the EHS is also a HS the release quantity is the RQ of the HS. In the event that the EHS is not a HS the release notification value is that value promulgated in the April 22, 1987 Final Rule (52 FR 13378 - 13410). However, there is a subtle difference between notification requirements of Section 304 and Section 103. In Section 304, notification must be made only if the release leaves or threatens to leave the perimeter of the facility, whereas in Section 103, notification to the NRC must be made if the release is into the environment. Thus, the perimeter of the facility is not a constraint for notification requirements under Section 103. EPA published the list of 402 EHS on November 17, 1986 (51 FR 41570 - 41592) in an Interim Final Rule, and on the same date, published an NPRM which proposed the addition of five substances to the list of EHS, and the deletion of 40 substances from the list of EHS (51 FR 41593 - 41594). The criteria that are the basis of the list of EHS are provided in Table 1.

On April 22, 1987, EPA published a Final Rule which revised the list of EHS to include four additional substances. The Agency had decided to retain the 40 substances proposed for deletion pending the development of criteria for determining additional health effects resulting from short-term exposure at specified levels. EPA intends to reassess these 40 chemicals when such criteria are available.

The Agency applied the criteria shown in Table 1 to the data base of chemicals contained in the Registry of Toxic Effects of Chemical Substances (RTECS) and applied the additional criterion that the EHS had to be in current production. In addition, the Agency included substances on the EHS list that did not meet all of the formal criteria discussed above, but are in high production and have caused death and injury in accidents.

There are currently 406 substances on the list of EHS of which 145 are also CERCLA HS. Therefore, 261 EHS are candidates for designation as HS.

The Agency is considering designating these 261 EHS as CERCLA HS to ensure that releases of these substances are reported to the NRC for possible response by the Federal government, and to protect the SUPERFUND against response costs associated with releases of non-designated HS.

The Toxic Chemicals. Another list of chemicals defined in SARA that the Agency is considering for designation purposes is the list of toxic chemicals defined in Section 313 of SARA (Toxic Chemical Release Forms) as those chemicals listed in Committee Print Number 99-169 of the Senate Committee on Environment and Public Works, titled "Toxic Chemicals Subject to Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986," including any revised version of the list as may be made pursuant to subsection (d) or (e) of Section 313 of Title III of SARA. The Administrator may by rule add a chemical if there is sufficient evidence to establish that: 1) the chemical is known to cause or can reasonably be anticipated to cause significant adverse acute human health effects at concentration levels that are reasonably likely to exist beyond facility site boundaries as a result of continuous, or frequently recurring releases; 2) the chemical is known to cause or can reasonably be anticipated to cause cancer in humans or teratogenic effects, or serious irreversible reproduction dysfunctions, neurological disorders, heritable genetic mutations, or other chronic health effects; or 3) the chemical is known to cause or can reasonably be expected to cause, because of its toxicity, its toxicity and persistence in the environment, or its toxicity and tendency to bioaccumulate in the environment, significant adverse effects on the environment of sufficient seriousness to cause reporting under Section 313 of Title III of SARA. In addition, any person may petition the Administrator to add a chemical to the list of toxic chemicals.

The owner or operator of a facility subject to the requirements of this section of Title III of SARA must complete a toxic chemical release form for each toxic chemical listed that was manufactured, processed, or otherwise used in quantities exceeding the toxic chemical threshold quantity defined in Section 313(f). Draft release forms have been distributed to the public for comment.

There are currently 329 substances on the SARA Section 313 toxic chemicals list. The Agency may designate some or all of the substances on this list as CERCLA HS.

The Hazardous Waste Site Substances. Section 110 of SARA (Health-Related Authorities) requires that the Administrators of both the EPA and the Agency for Toxic Substances and Disease Registry (ATSDR) prepare a list of at least 100 HS which are most commonly found at facilities on the National Priorities List (NPL) and which they determine are posing the most significant potential threat to human health due to their known or suspected toxicity to humans and the potential for human exposure to such substances at facilities on the NPL or at facilities to which a response to a release or a threatened release is under consideration. This section also provides for regular additions to this list. The Administrator of the ATSDR must prepare toxicological profiles of each of these substances.

The Agency may designate as hazardous those Section 110 substances that are not already HS to protect the Superfund against response costs associated with releases on non-designated chemicals.

Other Candidate Substances for Designation

In addition to the lists identified above that contain chemicals that are candidates for designation, the Agency has identified a number of other lists that may contain chemicals that should be designated as HS. These list include but are not limited to :

- The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) active ingredients;
- The Occupational Safety and Health Administration (OSHA) substances, i.e., those substances requiring a Material Safety Data Sheet.
- Carcinogens identified by the Carcinogen Assessment Group, the Office of Toxic Substances and other Agency offices, as well as those identified by the National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC); and

The Agency may develop a priority-setting process for selecting substances from the lists that are of greatest concern to the CERCLA program and focus its resources on those highest priority substances that are most likely to present a threat to public health or welfare or the environment. Criteria which could be applied to the lists of chemicals for purposes of prioritization includes degree of replication of a substances on various lists, the level of production of a substance, the RQ which would be assigned to a substance using the RQ Adjustment Methodology, the substances' history of release and the environmental mobility and persistency of a substance.

Options for Designation

The Agency is considering a number of options for implementing its designation strategy. It is cognizant of the regulatory burden imposed by designation, and at the same time is concerned that a number of chemicals are released or have the potential of being released which are not currently CERCLA HS, and therefore, are not reported at the federal level.

The Agency is currently considering several strategies for designation, including a limited designation strategy whereby only those chemicals on the lists identified above from SARA would be considered for designation, with emphasis on the Extremely Hazardous Substances. The Agency may further prioritize these lists to designate only the most dangerous of the chemicals. The Agency is also considering a broader designation methodology that would include other lists in addition to those from SARA as sources of candidate substances. These options will be presented and public comments solicited in an NPRM to be published in the latter part of 1987.

REFERENCES

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2. Technical Background Document to Support Rulemaking Pursuant to CERCLA Section 102, Volume 1. March 1985. Prepared under contract No. 68-03-3182 to the US Environmental Protection Agency.

3. Technical Background Document to Support Rulemaking Pursuant to CERCLA Section 102, Volume 2. August 1986. Prepared under contract No. 68-03-3182 to the US Environmental Protection Agency.

4. Technical Background Document to Support Rulemaking Pursuant to CERCLA Section 102, Volume 3. December 1986. Prepared under contract No. 68-03-3182 to the US Environmental Protection Agency.

Route of Exposure *	Acute Toxicity Measure **	Value
Inhalation	Median Lethal Concentration in Air (LC50).	Less than or equal to 0.5 milligrams per liter of air.
Dermal	Median Lethal Dose (LD50).	Less than or equal to 50 milligrams per kilogram of body weight.
Oral	Median Lethal Dose (LD50).	Less than or equal to 25 milligrams per kilograms of body weight.

Table 1. Criteria to Identify Acutely Toxic Chemicals that may Present Severe Health Hazards to Humans During a Chemical Accident or Other Emergency.

* The route by which the test animals absorbed the chemical, i.e. by breathing in air (inhalation), by absorbing it through the skin (dermal), or by ingestion (oral).

** LC50: The concentration of the chemical in air at which 50 percent of the test animals died. LD50: The dose which killed 50 percent of the test animals. In absence of LC50 or LD50 data, LClo or LDlo data should be used. LClo: Lethal Concentration Low, the lowest concentration in air at which any test animals died. LDlo: Lethal Dose Low, the lowest dose at which any test animals died.

THE EPA PERSONNEL PROTECTION TECHNOLOGY RESEARCH PROGRAM

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ABSTRACT

The Environmental Protection Agency's Personnel Protection Technology Research Program provides data, information and technology to enhance the Agency's capability to perform its mandated roles that require: 1) regulation of pesticides and toxic substance handling and use; and 2) operation of EPA and contractor personnel at chemical spills and uncontrolled hazardous waste sites. To meet this objective, the Program is developing, evaluating and improving chemical protective clothing and equipment; procedures to enhance the safety and cost-efficiency of working conditions; methods to predict the effectiveness of chemical protective clothing; and detection methods and devices that warn of imminent hazards to life and health.

INTRODUCTION

The Environmental Protection Agency's (EPA) Personnel Protection Technology Research Program supports the activities of the: 1) Office of Pesticide Programs (OPP) mandated by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), 2) Office of Toxic Substances (OTS) mandated by the Toxic Substances Control Act (TSCA) and 3) Office of Emergency and Remedial Response(OERR) mandated by the Superfund Amendments and Reauthorization Act (SARA or Superfund). The Program is principally funded by the Water Engineering Research Laboratory and the Hazardous Waste Engineering Research Laboratory (HWERL); HWERL provides technical management support.

Pursuant to FIFRA, OPP is responsible for developing agricultural protective clothing regulations, implementing the pesticide registration process, reviewing and approving pesticide labels, administering the pesticide-related Farm Safety Program, and supporting training and education programs for pesticide users through state extension services. These efforts are aimed at improving levels of protection for the estimated 4 million farmers, farm workers and farm families who may be directly and chronically exposed to pesticide sprays, dusts and ambient residues. Program research in this area currently focuses on evaluating the effectiveness of protective clothing for pesticide mixers, loaders, and applicators.

TSCA and subsequent regulations require that producers or importers of new chemicals submit a Premanufacture Notification (PMN) to OTS at least 90 days prior to beginning manufacture or distribution. OTS must review the PMN, which may include a description of the protective clothing and respirators to be used, within 90 days and determine whether production of the new chemical will result in unacceptable health or environmental risks. Program efforts in this area currently focus on developing improved methodologies (i.e., test methods, predictive methods, and integrated systems) to estimate the effectiveness of respirators and protective garments.

Under the provisions of SARA, the EPA performs a variety of roles that affect (or are affected by) personnel protection technology. These include procuring and using (both directly and through contractors) protective clothing and equipment for laboratory and field operations, developing and reviewing site safety plans, and preparing and presenting safety training courses for EPA employees and client organizations. Program efforts in this area focus on improving personnel protection technology in order to enhance the safety, range, and cost effectiveness of operations at Superfund sites.

All of the above research efforts are performed through contracts, cooperative agreements with state universities, interagency agreements, in-house projects, technology transfer workshops and active coordination with researchers, manufacturers and users in the personnel protection area. Through these mechanisms, the Program: 1) conducts desk-top, laboratory and field evaluations; 2) prepares guidance documents on the selection and appropriate uses of protective clothing and equipment; 3) evaluates, develops and verifies methods for predicting and testing the performance of these products; 4) analyzes the costs and benefits of alternative technologies; and 5) identifies research results that will significantly enhance EPA operations involving hazardous materials. Table 1 summarizes the outputs of these activities through June 1987.

RESEARCH IN SUPPORT OF FIFRA-MANDATED OPP ACTIVITIES

To support OPP's FIFRA-mandated responsibilities, the Personnel Protection Research Program has initiated research projects in three areas: laboratory evaluations and field tests of protective clothing effectiveness, and production of guidance manuals on the selection of protective clothing for agricultural pesticide operations.

Previous efforts by the OPP and others have confirmed that the hands are an important site of pesticide exposure, and research has demonstrated that chemicals can permeate "impermeable" gloves without degrading their physical characteristics. To aid OPP and pesticide users to identify gloves that will provide adequate protection, EPA contracted Arthur D. Little, Inc., to: 1) produce, assemble and evaluate data on the effectiveness of polymer gloves against pesticide exposures, and 2) identify correlations in the collected data that will facilitate glove selection. Three types of testing are being employed in this project: two "rapid screening" procedures to eliminate glove-chemical combinations that result in observable, rapid degradation of glove polymers and ASTM method F-739-85 to test for permeation.

Degradation tests on 92 pesticide-glove combinations have been completed and at least 60 combinations are being selected for subsequent permeation testing. Permeation tests on two pesticides are in progress. As the project proceeds, the two rapid screening tests will be compared and the more satisfactory will be selected for future use. Also, pesticides which have low water solubility and volatility do not lend themselves to the ASTM permeation test due to the difficulty of collecting the permeant after it has passed through the glove sample. An effort is underway to identify alternative methods for collecting the permeant.

Thermal comfort is a key factor in the selection of chemical protective garments for agricultural operations. Existing protective clothing provides a trade-off between thermal comfort and pesticide penetration resistance. To obtain a better understanding of this trade-off, EPA entered a cooperative agreement with the University of Tennessee under which 40 fabrics were screened for thermal comfort properties and 32 were tested for penetration resistance against four pesticide formulations: Dicofol, Ethion, Chlorobenzilate and Terrazole. The results of this work will be used to identify fabrics with superior combinations of thermal comfort and penetration resistance. These fabrics will be fabricated into coveralls and field tested by citrus and greenhouse workers as one part of a cooperative agreement between EPA and the University of Florida.

Under this agreement, the University of Florida is investigating the dermal pesticide exposure received by greenhouse workers and the mitigation of that exposure through the use of protective clothing. In phase I of the field test, raw data was collected by having pesticide sprayers wear collection patches on the inside and outside of their clothes. The patches were then removed and subjected to extraction and chemical analysis. In addition, pesticides were removed from the hands with ethanol rinses and breathing zone air was sampled. Approximately 3000 pesticide samples were generated in this phase, which included various application methods (e.g., tractor-drawn boom and span, handgun, pulse fog and drench spraying) in various settings (e.g., open, enclosed and partially enclosed greenhouses). In the second phase, begun in September 1986 and to be completed soon, the effectiveness of work pants, long-sleeved shirts, T-shirts and two commercial brands of coveralls will be evaluated. Field evaluations of the fabrics identified in the University of Tennessee study have also begun and will continue through 1988.

In addition to these field and laboratory evaluations, the Personnel Protection Research Program has also initiated development of a Guidance Manual for Selecting Protective Clothing for Agricultural Pesticide Operations, with Arthur D. Little, Inc., serving as the contractor on the project. In the first phase of this effort, an Interim Guidance Manual (IGM) was prepared as an internal resource document for the OPP. The IGM focuses on assessments of the effectiveness of polymer gloves against pesticide exposure and of the limitations, imposed by thermal comfort needs, on the use of protective garments in agricultural pesticide operations. The IGM has been circulated among the research and user community, and the scope of the final Guidance Manual will be based on their comments, and on those of OPP. Topics in the final version may include: work task functional requirements; manufacturing methods and materials; performance data; human factors data; product lists; decontamination agents and methods; and foot, eye, head, forearm/arm and respiratory protection.

RESEARCH IN SUPPORT OF TSCA-MANDATED OTS ACTIVITIES

Because OTS is limited to 90 days to complete a PMN review, and because they want to minimize additional testing by manufacturers, the Office requires reliable model(s) or system(s) for predicting the effectiveness of protective clothing and respirators in the workplace. Therefore, to support these needs, the Personnel Protection Research Program is evaluating and improving methods, equipment and procedures for estimating the exposure protection provided by these products. As methods are identified or developed, they are being incorporated into the PMN review process, giving OTS the opportunity to provide prompt feedback.

In the first phase of these model development efforts several theoretical permeation models and test methods for estimating permeation related properties were identified and compared to the results of permeation tests. The models and test methods chosen were based on theories of the solution thermodynamics of polymer/solvent systems and the diffusion of solvents in polymers. The contractor further developed these models and test methods to estimate the solubility (S) and the diffusion coefficient (D) for a solvent in a glove polymer. Given S and D, the permeation of a glove by a solvent can be predicted for various exposure conditions using analytical or numerical solutions to Fick's laws.

Based on this work, a computer model (written in Fortran and operable on an IBM PC) was developed and delivered to OTS for hands-on evaluation. Using simple inputs, this program can calculate S and D, and generate curves used in estimating the barrier effectiveness of protective garment materials. Also, the capabilities and reporting requirements of existing permeation test methods were analyzed and a preliminary hierarchy for test method specification was proposed. Analyses of immersion and vapor sorption tests are underway and development of a splash test method, in cooperation with standards development organizations, will be pursued in 1987. The results of these efforts, which will continue through 1989, will be integrated into a system that will enhance the performance of PMN reviews.

In addition to evaluating the effectiveness of protective clothing, OTS must also assess the likely effectiveness of any respirators included in a PMN. Research to enhance OTS capabilities in this area is being conducted through an interagency agreement with the National Institute for Occupational Safety and Health (NIOSH). This research will determine the workplace protection factors of respirators, develop laboratory test methods to predict these factors and establish a decision logic for OTS evaluation of PMN submittals involving respirators.

The initial phase of this work involved an assessment of quantitative fit test methods, which measure the effectiveness of a respirator by comparing the concentration of a test contaminant inside the facepiece to that outside. The reliability of this test is critical to meaningful measurements of workplace protection factors, and to individuals who use fit test data to select respirators. Laboratory evaluations demonstrated that the measured protection factor can be strongly biased by the position of the sampling probe and the location of leaks into the facepiece. Work in 1987 will focus on eliminating this bias.

RESEARCH IN SUPPORT OF SARA-MANDATED EPA ACTIVITIES

A number of Personnel Protection Research Program projects support SARA-related hazardous waste site cleanup and emergency spill response activities. These projects are identifying, evaluating and improving prototypical and commercially available chemical protective materials, clothing and equipment, and related procedures, that could potentially improve the safety, range, and cost-effectiveness of EPA and EPA-contractor operations at chemical spill and uncontrolled hazardous waste sites. Products of particular interest include disposable protective clothing, vital signs monitors, personal cooling devices, respiratory protection devices, new garment materials, totally encapsulating ensembles and personal communication devices.

Recent Program efforts to evaluate and improve protective clothing materials include an assessment of the stiffness and strength of Teflon^R/Nomex^R laminate (a newly available material resistant to a wide range of chemical compounds) at cold temperatures and an investigation of the permeation and degradation resistance of a 20 mil chlorinated polyethylene (CPE) to liquid chemicals. In the latter project, CPE swatches were exposed to ten chemicals (acetic acid, acetic anhydride, acetone, bis (2-chloroethyl) ether, carbon tetrachloride, ethylene diamine, isopropyl alcohol, nitrosodimethylamine, phenol and xylene) in order to determine permeation rates, breakthrough times and swelling. Mean permeation breakthrough times ranged from 0 to 170 $mg \cdot m^{-2} \cdot s^{-1}$, and swelling and solubility data also showed wide variation, depending upon the chemical. Soaking CPE test swatches in one chemical resulted in a loss of weight, while contact with four other compounds resulted in weight gains of over 100% by CPE. In eight out of ten cases chemical contact also reduced the capacity of CPE to resist tearing.

In an interagency effort with the U.S. Army's Chemical Research and Development Center, advanced development of a prototype, long-term (2.5 hour), self-contained, chemical protective ensemble (based on an existing Army/Coast Guard prototype) was pursued. The ensemble development was performed by USD Corporation. Some desirable modifications (e.g., lighter weight, simplified maintenance and 2.5-hr service life) were attained, but the breathing apparatus failed NIOSH certification testing twice. No additional attempts to obtain certification are planned. In related projects, the high pressure oxygen compatibility of the apparatus' materials of construction and the state-of-knowledge of the physiological effects of routinely breathing high concentrations of oxygen were evaluated.

Other recently completed Program efforts to improve equipment include a preliminary investigation of critical design features of back-mounted equipment (to minimize risk of back injuries) and a field evaluation of three recently developed vital signs monitors, which are used in heat stress management programs at site cleanup operations. This evaluation was conducted at a dioxin cleanup site in Missouri to assess the monitors' ease of use, suitability for field operations and accuracy. Further evaluations of vital signs monitors and evaluations of personal cooling systems are planned for early 1987 in order to develop modified heat stress management work practices.

Also in 1987, a project will begin to identify and evaluate commercially available or prototypical personal hazard detectors. This effort will involve desk-top, laboratory and field evaluations of personal toxic gas, combustible gas and oxygen deficiency detectors. Evaluation criteria will include reliability, ease of use, sensitivity, portability, cost and safety. Initial results indicate that, under field conditions, currently available detectors exhibit some generic failure modes: failure below 0°C and in precipitation, lack of portability and sensitivity, and selectivity (or lack thereof).

With regard to evaluating and improving personnel protective procedures for Superfund operations, two Program efforts are underway: development of a field test kit for protective clothing and evaluation of decontamination agents and methods. The field test kit has been laboratory tested and the results compared to those obtained using ASTM Method F-739-85 (permeation test method). Three kits are undergoing field testing by EPA response groups. The kit is relatively inexpensive and readily field usable: Liquid waste is placed in a shallow cup, the cup is covered by a swatch of clothing material and inverted, and the rate of permeation is monitored gravimetrically using a two-place, battery-powered balance.

COORDINATION ACTIVITIES

In a critically important set of activities, the Personnel Protection Research Program continually promotes the transfer -- both inward and outward -- of information on personnel protection research needs, activities, plans and outputs; analyzes EPA needs in this area; and sponsors investigations of the state-of-the-art in this field. Specific coordination and technology transfer activities in 1987 will include: continuing active participation in ASTM Committee F-23 on Protective Clothing, making presentations on research progress at the Second International Symposium on the Performance of Protective Clothing and the American Industrial Hygiene Conference, participating in an Interagency Memorandum of Understanding Work Group with representatives of the U.S. Coast Guard, NIOSH, Occupational Safety and Health Administration and Federal Emergency Management Agency; conducting a second intra-EPA Workshop on Personnel Protection Research and Research Needs; and participating on the American Conference of Governmental Industrial Hygienists Committee on Agricultural Health and Safety.

Similar activities are planned at least through 1991, and are expected to continue to provide ideas and information of value to the planning and performance of personnel protection research in support of EPA's needs.

TABLE 1. SUMMARY OF EPA PERSONNEL PROTECTION PROGRAM OUTPUTS

Title	Product Type*	Date
Long-term, Self-contained Chemical Protective Ensemble elf- ined	CP	5/84
Decontamination Techniques for Mobile Response Equipment Used at Waste Sites	PR,S	8/85
Evaluation of Chlorinated Polyethylene Protective Garment Material	PR,S	12/85
Test Methods to Predict the Permeation of Polymers by Organic Solvents	CP	1/86
Interim Protocol for Diving Operations in Contaminated Water	PR,S	8/86
Predicting the Effectiveness of Chemical Protective Clothing-- Model and Test Method Development	PR,S	9/86
Biases Associated with In-facepiece Sampling of Respirators	PR,S	9/86
Interim Guidance Manual for Selecting Protective Clothing for Agricultural Pesticide Operations	IR OP	9/86 6/87
Review of Models for Predicting the Effectiveness of Protective Clothing	IR	12/86
Effect of Fabric Weight and Thickness on Pesticide Penetration	CP	1/87
Evaluation of Protective Clothing for Agricultural Pesticide Operations	CP	1/87
Predicting Breakthrough of Chemicals through Protective Clothing	CP	1/87
Field Evaluation of Protective Clothing: Experimental Design	CP	1/87
Field Test Method to Evaluate Protective Clothing	CP	2/87
Interpretation of the Results of Permeation Testing	OP	6/87
Evaluation of Protective Gloves Used in Agricultural Pesticide Operations	OP	6/87

*OP = oral presentation, CP = article in conference proceedings, PR,S = project report and summary, and IR = internal report

APPLICATION OPPORTUNITIES FOR CANINE OLFACTION: EQUIPMENT DECONTAMINATION AND LEAKING TANKS

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ABSTRACT

Rapid screening of heavy equipment used in site cleanup for residual contamination and scanning of underground storage tanks for leaks were identified as two promising environmental applications for canine olfaction.

In equipment decontamination, the objective was to demonstrate that a trained dog could detect and indicate extremely small residues of hazardous chemicals remaining on heavy equipment such as bulldozers, backhoes and front end loaders after washup. Using xylene and 1,1,1-trichloroethane as models of common hazardous chemicals, a trained dog reliably indicated hidden samples emitting as little as 0.5 ug/min. Gaussian dispersion models indicated that the dog is detecting 5-10 ppt or less at these emission rates. Field tests on equipment indicated detection at emission rates as low as 1 ng/min.

From tests to evaluate the dog's ability to differentiate similar compounds, it was concluded that, at least in some compound families, the dog does respond to both the compound used for training and its congeners. This capability may be useful in finding any members of such families at a site.

Gasoline was selected as the material of greatest importance when searching for underground leaks. Water-washed gasoline, used to simulate underground leaks, did exhibit minor changes in composition. However, possibly due to the training approach used, the dog was unable to differentiate the washed gas from unwashed gasoline. Alternate approaches are delineated for future study.

INTRODUCTION

Passage of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA), commonly known as Superfund, and most recently, the Superfund Amendments and Reauthorization Act of 1986 (SARA), has placed great emphasis on the cleanup of hazardous waste sites and spills. Careful and complete delineation and monitoring of such sites, both before and after cleanup, have become increasingly important. The cost and complexity of such monitoring programs have been far from inconsequential and have led to the development, testing, and use of highly sophisticated analytical equipment to provide more reliable results more quickly and at lower ambient levels. In some cases, however, highly sophisticated technology is used solely because it is the only or the fastest approach accepted by the technical and regulatory community, even when precise data are not needed.

In 1983, an alternate, innovative approach to monitoring was brought to the attention of the Edison, NJ Releases Control Branch of EPA's Hazardous Waste Environmental Research Laboratory (Cincinnati). The technique, canine olfaction, has attained wide acceptance as an aid to the military, to police, to rescue workers, to custom agents, and to certain industries to detect explosives, weapons, personnel, narcotics, leaking gas, underground pockets of leaking cable oils, and even termites, often under conditions WHERE NO OTHER TECHNOLOGY IS EQUALLY CAPABLE. In some of these areas, the dog remains the "state-of-the-art".

The results of a preliminary study funded by US EPA's Releases Control Branch in 1983 to study the feasibility of the technique and the breadth of its potential applications essentially confirmed expectations (1). The dog was, if anything, more sensitive to chemical vapors than expected, detecting "plumes" from miniscule samples at considerable distances and tracking them back to their sources; potentially providing environmental workers with a tool to zero in on contamination very quickly so that quantitation could then be carried out in the most cost-effective manner and without numerous "not detected" results. A great deal also was learned about the techniques suitable for training dogs for such work, environmental situations where a dog might be useful and the reluctance of regulators, contractors, analysts, and others accustomed to dealing with instruments and numerical results.

The current Cooperative Agreement (2) between the USEPA and the New Jersey Institute of Technology was undertaken to explore the dog's ability to work usefully in two different areas of considerable interest to USEPA, cleanup contractors, and state agencies. These two problem areas were:

1. Assessing the effectiveness of heavy equipment decontamination after use at a site; and

2. Non-invasive screening for leaks from underground storage tanks (UST), particularly those containing gasoline.

While there have been no applications of the dog in the environmental field per se, there have been a number of reports that really fit this category. Dogs were used to detect 150 leaks, some too small to confirm with conventional instrumentation, over the 94 mile length of a new natural gas pipeline across Canada, all within a two-week period (3). They also were used to locate leaks of electrical cable oils below the paved streets of New York City (4). Experiments have even demonstrated that dogs were able to detect nitrogen, Freon, and helium gas emanating from a manifold system (5).

For the two phases of this project, "decontamination" and "UST", two chemicals were selected to represent hazardous materials commonly encountered at sites. These were m-xylene and 1,1,1-trichloroethane (TCE). Xylene was chosen as a less volatile, less toxic representative of the aromatic solvents benzene and toluene frequently encountered at spills and cleanup sites. Of course, xylene is also a component of gasoline and fuel oil. Similarly, the non-carcinogenic trichloroethane was chosen to represent the chlorinated hydrocarbons frequently found in contaminated groundwater and attributed to industrial degreasing operations.

The project was carried out with one primary dog, a 5-year old German Shepherd Dog, Ramos, who had already demonstrated his ability and desire to do scent work in other areas. Ramos was trained and handled by Mr. L. Don Arner. A second dog, a female German Shepherd Dog named Anja, and her handler, Mr. Don Bowman, were brought into the project later for specific segments.

The training protocol relied on positive reinforcement (reward of some type) for all successes, no matter how slight and the withholding of reward for failure (negative reinforcement). Rarely if ever was discipline (aversion training) necessary. The training further used a technique called "chaining" in which each small segment of the training is taught separately and only combined as the dog succeeds with the first effort. For example, the dog learns to search, he learns to detect a specific odor, he learns to respond by pawing or retrieving. Each dog was taught to recognize a particular scent, that of the target chemical, by introducing the dog to a somewhat higher level of the chemical (up to 0.5 gm) protected in a hollow wooden dowel or a 35 mm film canister and rewarding the dog for the very first alert or recognition. The amount of chemical was then rapidly reduced and/or the difficulty of finding the source of the chemical was increased. In fact, the dog quickly learned to recognize and detect both target chemicals (TCE, xylene), even when the source was reduced to one drop (about 0.05 gm). Because of the project's goals, the objective was to develop the dog's ability to detect low concentrations of the vapor rather than his ability to recognize aged samples or track an aged scent great distances, as had been demonstrated in the earlier study.

Calculations using a simple Gaussian air dispersion model (6) were carried out to provide some insight into the airborne level of chemicals the dog might be perceiving at different distances from a source. These calculations suggested that with a source emitting at 0.5 ug/min in a 5 mph breeze the dog could be responding to as little as 1-5 parts per trillion in the air, depending on how far from the source he gave the first alert. Figure 1 is a plot for such a model calculation. Laboratory research by other investigators has indicated that the dog was capable of detecting chemical odors at the parts per quadrillion level (7).

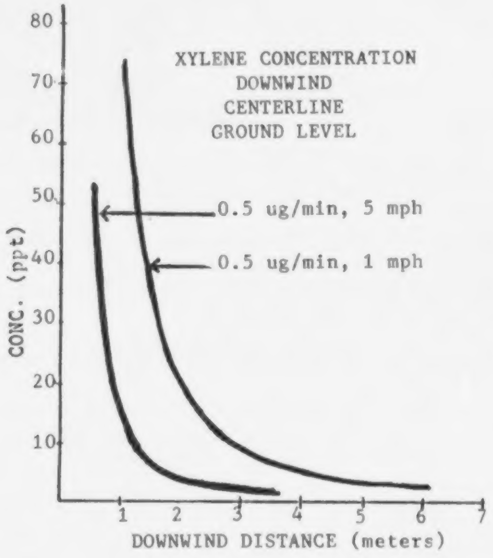

Figure 1. Calculated plume concentrations for xylene.

To work at even lower emission levels and also to provide a constant emission rate, as might be expected from a contaminated piece of heavy equipment or a tank leak, permeation tubes, consisting of sealed lengths of plastic that allow vapors to permeate through the walls at uniform rates as long as liquid is present (Figure 2). These efforts did not deter the dogs. Ramos readily and happily found permeation tubes emitting at only 0.4 ug/min, the practical limit for calibration by weight loss over a reasonable length of time. Even a commercial tube calibrated as emitting xylene at 10 ug/min at 90 C (the calculated emission rate at 25 C is only 0.062 ug/min) was readily found by both dogs. Of course, the tubes were never handled without gloves and were never touched by the dogs to avoid imparting other scents as clues. From later work, it appears that the dog is probably still one or more orders of magnitude away from the CANINE DETECTION LIMIT!

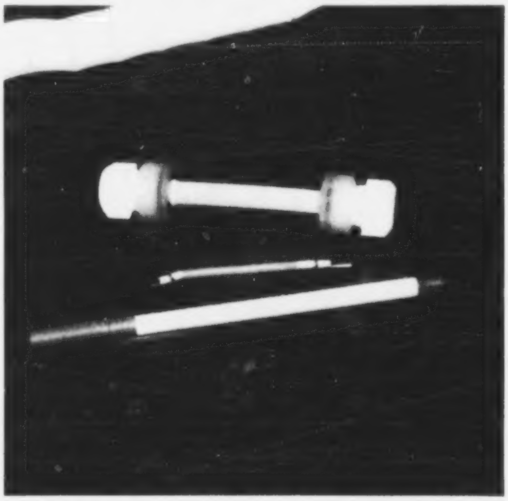

Figure 2. Permeation tubes used in training.

DECONTAMINATION

To familiarize the dog with the type of searches that could be encountered, samples, either a drop on a surface or in a dowel or film canister, or permeation tubes, were hidden on, under, or in "available" heavy equipment vehicles. The dog was then brought to the site and encouraged to search, usually first "scanning" the entire vehicle on his own and then proceeding to a more detailed search under the guidance of the handler. With rare exception, the article was located quickly.

To simulate a real situation, permission was obtained to use a front end loader at a construction site in Morris Plains, New Jersey. A mud consisting of 5 g of alumina powder, water, and xylene was applied to a spot on the vehicle and the dog brought in to search. Blanks consisting only of alumina plus water were also applied. This sequence was repeated three times, placing the xylene-tainted mud at different points. In the first test, the dog localized the odor but did not actually locate the sample, which was on the underside of the beam supporting the shovel. In the second test, the dog found the sample (in the opening of one of the lower frame members) after considerable searching and with some guidance. In the third test, the dog quickly found the sample on a horizontal surface at the rear of the left track. (Figure 3)

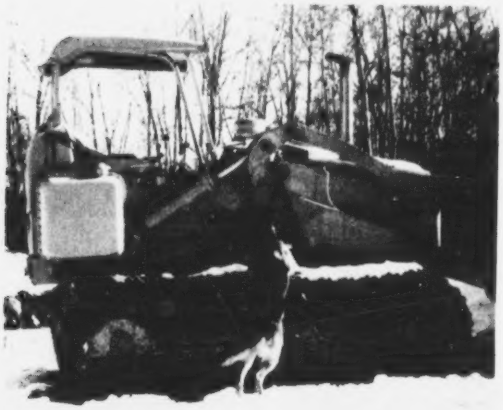

Figure 3. Ramos searching vehicle.

Throughout the tests, it was observed that the dog was very anxious to get underneath the vehicle. This behavior plus a strong diesel fuel odor led the investigators to discover a very significant fuel oil leak from a ruptured line. Diesel fuel had saturated the ground under the vehicle and it was this odor that the dog was concentrating on. Since diesel fuel is rich in xylene, the dog's success in locating added sources becomes even more amazing. Even more intriguing was the dog's considerable interest in the front bumper of one investigator's car during a rest period. A sample alumina/xylene mud had been placed on the bumper the day before as practice.

To obtain a semi-quantitative idea of the level of xylene that the dog was detecting in these tests, air samples were collected directly from each mud immediately after the dog had completed his search, as well as from the general area (background). The sample from test 2 was lost when the dog pawed it. These samples were collected by holding an inverted 2.5" funnel 0.5-1.0 inches over the mud and drawing air into a Tenax adsorbent trap for 10 minutes at 3-4 cc/min (Figure 4).

Figure 4. Equipment used to collect air sample over alumina mud.

The traps were then returned to the laboratory, desorbed thermally, and analyzed by gas chromatography (GC), giving the levels of xylene noted in Table 1.

TABLE 1. DETECTED XYLENE CONCENTRATIONS

Sample	Conc. (ppb)	Emission Rate (ng/min)
background	10	0.3
sample.#1	68*	1.0
sample.#2	LOST	-
sample.#3	24	0.77
car bumper	517	16.0

*sample funnel contaminated with mud, result high.

It must be concluded that the dog is able to detect and locate a source of xylene (simulated residual contamination in this case) -- even when a significant amount of the same vapor is present in the background air.

In a second set of experiments at another location, xylene-contaminated alumina muds were applied to two of five hand-shovels placed on snow-covered ground and a blank water/alumina mud was applied to a third one. The dog found one xylene sample (A) rapidly, but he showed little interest in the second xylene sample (B) until directed to search that shovel. The dog also did show considerable interest in the blank shovel (C), but not at the mud itself. Instead, his interest seemed to be concentrated on an area to which some of the melting snow and mud may have run. Air samples were again taken and analyzed by GC. While the GC of the air trapped over the blank shovel showed no xylene, there was another, as yet unidentified, peak.

TABLE 2. XYLENE DETECTION ON SHOVELS

Sample	Conc. (ppb)	Emission Rate (ng/min)
shovel A	23	3.6
shovel B	11	0.2
Blank C	0	0
background	0	-

On the basis of these experiments, it appears that the dog can be a valuable asset to EPA and cleanup contractors trying to establish whether equipment can be removed from a site. Since the decision to use the dog and the selection of the target compound can be made while the cleanup is proceeding, there would be more than adequate time to train or condition the dog to the compound(s) of interest. And, as noted earlier, the dog would be used only to point out residual contamination, whether on heavy equipment, hand tools, or even personnel protective gear. It remains the responsibility of the cleanup crew to clean the indicated area further or "measure" the dog's find by wipe tests and quantification.

CHEMICAL DISCRIMINATION

One question kept surfacing as work progressed. How selective was the dog? Would 129 dogs be needed to find the 129 priority pollutants (and more for each chemical on the RCRA lists) or could one dog find them all? And, from the opposite point of view, would a dog trained to find, for example, xylene, give false positives by also finding Parathion, trichloroethane, acetic acid, diesel fuel, and anything else in the area? These were interesting questions and the team set out to get some insight into what would happen.

Field-testing the question of selectivity presented a unique problem. It was realized that while the goal was to observe the dog's natural response (retrieve, curious, ignore, etc.) to any new chemical that had not previously been used in training, this natural response would soon be replaced by a trained or learned response. For example, rewarding the dog for finding substances other than the original target (trained) chemical would be training him; discipline also would be training him (aversion training) not to indicate those. Even no reaction by the handler to "an improper find" could cause the dog to work harder to gain approval -- by seeking more of the same odor! Consequently, it was anticipated that only limited testing could be done before a learned response would be produced.

The initial experiments consisted of choices between structurally-similar chemicals, xylene and ethyl benzene, or trichloroethane and trichloroethylene, placed on undisturbed twigs several feet apart. Human odor thresholds for the chlorinated hydrocarbons are higher (less sensitive) than for the aromatics (Table 3). With xylene and ethyl benzene

TABLE 3. CHEMICAL ODOR THRESHOLDS

Chemical	Threshold (ppm)
trichloroethane	20.0
trichloroethylene	20.0
toluene	2.0
xylene	0.5
ethyl benzene	2.0
n-amyl alcohol	5.0

the first reaction to the ethyl benzene appeared to be recognition that the odor was "interesting (i.e., similar) but not quite right". However, in repeat tests the dog then did retrieve articles tainted with ethyl benzene, probably the learned behavior expected from the noted unintentional training. In experiments with chlorinated compounds, the dog initially ignored the trichloroethylene, but began to show awareness in subsequent experiments. The tendency to retrieve trichloroethylene articles never was as strong as that for ethyl benzene.

In a more complex experiment, undisturbed twigs 2-3 feet apart were impregnated with 1 drop of water, amyl alcohol (dissimilar odor), xylene, and ethyl benzene. When allowed to explore the area freely, the dog noted but ignored the amyl alcohol, showed considerable interest (and uncertainty?) about the ethyl benzene, and ultimately retrieved the xylene.

Because of concern about "incidental training", this question of selectivity was not pursued further. It was the research team's opinion that the find of any contamination close in character to that of the target material would be useful and worth investigation. And, while it was unlikely that a completely different chemical odor would be present at a site, if it was, monitoring personnel should be interested in knowing of its presence.

Thus, after several months of developing and modifying field techniques the program had produced a dog that could be reliably used to locate small residues of chemicals such as might persist on heavy equipment even after decontamination. Where wipe tests only have a random probability of "hitting" a contaminated spot, the dog could assist the contractor by quickly indicating where such residues were -- even when inaccessible or invisible to human observation -- and could quickly evaluate the effectiveness of subsequent cleaning attempts. Of course, the results of wipe or other tests at residues detected by the dog could, at some point, be interpreted as "de minimus" because of level or size of the area.

LEAKING UNDERGROUND TANKS

The area of leaking underground tanks was, as anticipated, a much more challenging problem. The goal was to use the intelligence and olfactory acuity of the dog to detect any vapors rising to the surface from a leak, as reported with leaks from buried natural gas lines and electrical cable oils. The concern was, however, that the dog would also find any other sources of the target compound, including every surface spill, drips at loading valves, etc.

In seeking means to avoid this problem, it was realized that while pure chemicals stored in tanks would not change when leaked, a complex mixture such as gasoline might undergo significant extraction and/or fractionation as the vapors from a leak permeated through the soil to the surface. Such changes could, it was hypothesized, provide a vapor profile sufficiently different from that of surface spills so that the dog could differentiate the two. Attempts to simulate this permeation phenomenon by analyzing gasoline vapors passing up through soil columns were not successful. Very little vapor was produced and no significant differences in profile were observed.

In an alternate approach, regular unleaded gasoline was extracted with water. Gas chromatographic analysis of the washed gasoline did indicate a reduction in the lower aromatics, benzene, toluene, and xylene. Efforts were then directed to training the dog Ramos to detect this difference, primarily the ABSENCE of xylene, with which he was familiar. In spite of several approaches and many attempts, however, a reliable, preferential response by the dog to the washed gasoline was never achieved. To this time it has not been possible to devise a training scheme or a search protocol that would provide the desired selective detection for vapors leaking from an underground tank.

It is unlikely that we will be able to solve this problem within the constraints of this project, and three challenging questions remain. First, the dog used in the gasoline work had, unfortunately, already been trained to detect xylene. Perhaps a dog without that training would be more sensitive to the different profiles of washed and unwashed gasoline (the xylene is not totally removed by extraction). The second dog, now being trained only for chlorinated hydrocarbons, may offer the opportunity to test this point.

Second, to date the dog has been asked to identify -- and differentiate -- the vapors emanating from small (1-2 drops) liquid samples of washed and unwashed gasoline. However, gas chromatography suggests that there may be significant and rapid changes in the vapor profiles over these samples that would not be comparable to the "steady state" that would exist over an underground tank leak. Diffusion tubes, vials equipped with small-bore vents, should provide more uniform vapor profiles for washed and unwashed gasoline that may be more readily differentiated by the dog. Unfortunately, preliminary gas chromatographic analyses exhibit no differences in the vapor profiles for the two samples.

Third, the investigators' experience, and conversations with other trainers, animal psychologists, and veterinarians have failed to uncover any prior evidence that an animal can be trained to respond to the ABSENCE of a stimulus. If that is true, a completely different training approach may be needed. One such approach would be the introduction of small amounts of marker chemicals. While it is expected that a dog would find a properly selected marker at the right concentration, just as dogs found the butyl mercaptan marker in natural gas, supplier resistance to contamination of their products at any concentration is anticipated. In addition, all surface leaks, spills and other sources at a site would soon become contaminated and would, presumably, be indicated by the dog.

CONCLUSIONS

1. The dog/handler team is a viable tool for EPA and their cleanup contractors to use in evaluating the effectiveness of decontamination efforts on equipment. Presumably, the effectiveness of cleanup of building surfaces as well as land sites, hand tools, and protective gear could also be evaluated by the dog.

2. The dog shows a degree of selectivity for similar compounds that is useful but not absolute. Greater selectivity could, presumably, be achieved by training, but it is doubtful if that would have any advantage.

3. A viable technique for using the dog to detect gasoline vapors from leaking underground tanks only has not yet been developed.

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NONDESTRUCTIVE TESTING (NDT) FOR LOCATION OF CONTAINERS BURIED IN SOIL

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ABSTRACT

At the 12th Annual Hazardous Waste Research Symposium held at Cincinnati in 1986 the authors reported on their work concerning the nondestructive testing (NDT) for location of containers buried in soil. An overall view was presented at that time. In this paper more detail is given about certain aspects of the testing, which could not be included previously due to space limitations.

Experimental work is described where seven techniques were reduced to four for the majority of the testing. (Originally 17 techniques were considered - 10 were eliminated during the literature search.) The four techniques:

- metal detector (MD)
- electromagnetic induction (EMI)
- magnetometer (MAG)
- ground probing radar (GPR)

were looked at in considerable detail. In particular, results concerning the ability of each method to detect the container(s) when not travelling directly over the container(s) (the lateral scan sensitivity) are given. Also detailed results, in the form of response contour diagrams, are given in the case of a "metal trash dump."

The effect of steel container burial orientation on the GPR is presented. Water table depth determination (to 15 feet) with GPR is also demonstrated. Under near perfect conditions of very little interference (i.e., low electrical conductivity, highly homogeneous, dry soil and absence of power lines, metal objects etc.), it is possible to detect empty plastic drums to a depth of three feet with EMI.

INTRODUCTION

An overview of the results of our work concerning the location of buried containers using various nondestructive (remote sensing) techniques were presented at the 12th Annual Hazardous Waste Research Symposium (Lord and Koerner, 1986a). This paper briefly reviews that work and presents additional detail concerning portions of the work which could not be presented earlier due to space limitations.

The investigation of subsurface objects can be approached in two very different ways. The first type is by use of a suitable destructive test method. This category includes: test pits, excavation trenches, auger holes, core borings, and observation wells. While one does indeed "see" the subsurface materials as they are excavated for ease of examination of subsequent testing, such methods have certain drawbacks in identifying and locating buried containers (Lord and Koerner, 1986a).

The second type of approach to identify and locate buried containers is by the use of a suitable non-destructive testing (NDT) method. These have also been called remote sensing or short range geophysical techniques. Within this category are the following methods which have either been used or appear to have applicability:

seismic reflection, seismic refraction, electrical resistivity, electromagnetic induction, induced polarization, metal detector, magnetometer, continuous microwave, pulsed radio frequency (ground penetrating radar), infrared radiation, sonar (pulse echo acoustic), electrical self potential, optical (below water surfaces), and penetrating radiation. All of the above methods are not equally suited for identifying and locating buried containers. Seventeen techniques were identified; as a result of the literature search ten were eliminated from further consideration; seven were evaluated further in the experimental phase of the project and are described in the following paragraphs.

DESCRIPTION OF METHODS

The metal detector (MD) and electromagnetic induction (EMI) methods are both inductive methods. A transmitting coil sends a continuous electromagnetic signal to a receiving coil. As a simplified description, the signal arrives at the receiver essentially through two major paths. One path is through the air and the induced signal does not change with the search position. The other path is through the subsurface material and is affected mainly by the local electrical conductivity of material involved. If an anomaly in the subsurface conductivity is encountered, e.g., a buried metal drum, the induced signal received through the earth path is changed significantly and the instrument indicates this change accordingly. Refer to Lord, et al. (1982a) and McNeill (1982), where the commercially-available instruments used in these studies are described in detail.

The ground penetrating radar (GPR) method operates on exactly the same principle as ordinary aircraft radar. A short pulse of electromagnetic radiation is beamed in the ground by a special highly-damped antenna and reflections occur from any subsurface discontinuity in dielectric constant. The reflected pulse arrives back at the receiving antenna and a display of reflected intensity versus depth is presented on an oscilloscope and on a recorder. This commercially-available technique is described more fully in Bowders, et al. (1982).

The magnetometer (MAG) method measures the local magnetic field strength (essentially the earth's field) and, with it, any changes in this magnetic field. The type used in this study was a proton precession model. The local magnetic field is determined by measuring the precession frequency of the proton magnetic moment. This rate is linear in the magnetic field and, as the frequency can be measured very precisely, the magnetic field can also be measured very accurately. (The source of precessing protons is an organic liquid; the liquid, generator and associated frequency measuring apparatus are contained in the MAG unit). A steel drum, being ferromagnetic, changes the local value from the earth's magnetic field and hence can be detected. The MAG technique (commercially-available) is described in more detail in Tyagi, et al. (1983).

The electrical resistivity (ER) method applies current to the ground through electrodes and depends, for its operation, on the fact that any subsurface variation in conductivity alters the form of the current flow within the earth. Therefore, the distribution of electrical potential is affected. The degree to which the potential measured at the surface is affected depends on the size, shape, location and electrical resistivity of the sub-surface mass. It is therefore possible to obtain information about the sub-surface distribution of various bodies at the surface. This method is used extensively in the oil and mineral prospecting area, but has not been widely used in shallow monitoring for small buried objects. It has seen some use for tracing sub-surface liquids. There are many sources of commercial equipment to choose from.

Seismic refraction (SR) is a well established geophysical method. In this method a seismic impulse (a hammer blow or explosive charge) is applied to the ground and the time to reach a transducer is measured for varying distances between the impulse and the transducer. The time is plotted as a function of distance and, if there is a well-defined stratigraphic layer beneath the surface, a characteristic break in the curve is found from which the depth to the layer can be determined. This method has not been used to detect small objects but is widely used in oil and mineral prospecting and exploration, and can be used to determine generalized topography at a dump site. Details concerning ER and SR can be found in the book by

Dobrin (1976).

The continuous microwave (CWM) method is similar to ground probing radar except that a continuous wave (CW) is used. The CW is swept in frequency and the wave reflected from the ground surface and the wave from a subsurface reflection interfere with each other. The spacing (in frequency) between the interference maxima (or minima) as the frequency is swept gives the depth of the reflecting surface. Some systems of this type are in an advanced research stage; however, they are not available commercially as far as the authors are aware. Details concerning this method are found in Koerner, et al. (1978).

DESCRIPTION OF FIELD SITES

The first site was in a nearly ideal dry sandy soil in an open field free of man-made interference (Lord, et al. 1982b). This site provided an excellent starting point for our experimental work. Three methods (ER, SR and CWM) were eliminated from further consideration based on the field data at this first site. The second site was much more formidable. (Koerner, et al., 1982) Here a saturated silty clay soil overlying shallow shale rock was used. Recognizing that containers are sometimes dumped directly into water (Weston, 1981) and that the salinity of the water can range from fresh to brine, the third study was directed at drums under water (Lord, et al., 1984).

Important is the extent to which ground water salinity influences the detection capability of these NDT methods. To this end, studies were made at a fourth site with steel containers buried in a soil of varying electrical conductivity. (Koerner, et al., 1984) The ocean was used as an electrical conductivity extreme and the conductivity decreased substantially as the survey moved inland. Site 5 was the same location as Site 4 but, in this case, plastic containers were used instead of steel. (Lord and Koerner, 1986b)

RESULTS

Overall View

Table 1 is an overall view of the ability of all four NDT methods to detect steel and plastic containers in a wide variety of subsurface situations. It should be considered as a guide to the practitioner when considering the use of NDT methods for a particular soil. (More detail can be found in last year's Conference Proceedings- Lord and Koerner, 1986a and the Final Report on the Project- Lord and Koerner, 1987).

Elimination of Certain NDT Methods

Figure 1 shows the results for a seismic refraction (SR) survey over the four steel drum pattern indicated on the figure. The drums were placed horizontally and with about four feet of soil cover at Site 1. There is essentially no indication of the drums in the survey. This experimental result, taken together with the fact that no work has been reported using seismic refraction (SR) in very short range container searching eliminated the technique from further consideration.

Figure 2 shows the results of an electrical resistivity (ER) survey over the same four steel drum pattern. Again there is no indication of the buried drums, even though the electrode spacing was choosen to be quite sensitive to the scale of the burial. The large increase at the right end of the survey corresponds to a gulley where water runs during rain storms. Thus for the same reason as with SR, this method was eliminated from further consideration.

Figure 3 shows the results of a continuous microwave (CWM) scan over the same four steel drum pattern. There seems to be an indication of the drums. However the calculated depths are too low by a factor of 3-4. Thus the method appears to be of quite limited value in searching for buried drums. As there were also no published reports of its use in this type application, the CWM method was eliminated from future consideration. A prime reason for the elimination of the three methods described above in this section is that there appeared to be much more attractive methods available, namely, MD, EMI, MAG, and GPR.

Location of a "Trash Dump"

At Site 1 a pit approximately 12 ft x 12 ft x 5 ft deep was filled with six steel drums, two plastic drums of various sizes and a few steel plates of various sizes. This site was called the "Trash Dump". Figure 4 shows the disposition of the buried objects. The responses of the four NDT methods over the "Trash Dump" are shown in Figures 5-8.

Figure 5 gives the MD results in terms of the strong response region. MD certainly detects the "Trash Dump" quite well.

Figure 6 gives the EMI results in terms of equal response amplitude contour lines. Note the position of the "posts" outlining the burial. Again, EMI locates the "Trash Dump" very well.

The MAG response is shown in Figure 7 again in terms of response contour lines. The center of the contour appears somewhat east (about 4-6 feet) of the center of the steel drum distribution. This characteristic of the MAG response is quite typical, but would not seem to be a serious drawback in the use of the method, for the "Trash Dump" is still located quite well.

Figure 8 shows the GPR response over the "Trash Dump". Here the side walls of the excavations are clearly seen, however the individual objects in the "dump" cannot be delineated. This is an extremely important use of the GPR method, i.e., to locate the side walls of a burial site.

Lateral Scan Sensitivity and Drum Orientation Effects

It is important to know how close the scan line must be to the actual buried container before detection if possible. Figure 9 shows the results of EMI scans at various distances laterally displaced from the line centered on the four 55-gallon steel drum sequence. The drums were buried at Site 1 with about four feet of soil cover. It is seen that the method is quite sensitive until the offset is greater than 8 feet for the antenna perpendicular to the center line and greater than 4 feet offset for the antenna parallel to the center line of the drums.

Figure 10 indicates the lateral scan sensitivity of the MAG method for a single 30-gallon steel drum buried at Site 1, with about three feet of soil cover, and at different orientations. The MAG method is sensitive to about 8 feet of lateral offset for single drums.

Figure 11 shows that the GPR method loses location ability if the scan is displaced by two feet from the center of the drum. The MD is a less sensitive version of EMI and hence has, as was shown in our experiments, very little lateral scan sensitivity.

Of interest also is the effect of steel drum orientation on the response of the various methods. The MAG results are shown in Figure 10. EMI results are shown in Figure 12. Figure 13 shows the effect of drum orientation on the GPR response. The MD does not have the requisite sensitivity to be very sensitive to drum orientation.

In summary EMI and MAG are moderately dependent on the orientation of the drum whereas GPR is extremely sensitive to orientation with the horizontal burial giving by far the best response.

Water Table Determination

Figure 14 shows the detection of the water table at Site 4. The varying depth water table here was of quite high electrical conductivity, so contrast was quite high and the table could be seen very easily to sixteen feet. The soil was a sand of very little stratigraphy, so the GPR method worked very well. This is, one of the deepest water tables that has been reported using GPR, to the authors' knowledge.

Detection of Plastic Drum with EMI

Figure 15 shows the results of EMI scans over 40 gallon empty plastic drums at Site 1. The drum at one and three feet of cover are easily detected, even with many feet of lateral offset of the instrument. In essence the EMI is acting like an air-void detector here. The excellent resolving power here is undoubtedly due to the fact that the sand is very dry, very uniform and of quite low electrical conductivity.

SUMMARY

The basic results of our work have been presented in detail elsewhere (Lord and Koerner 1986, 1987). The summary is given in Table 1. Here is presented a "pot pourri" of interesting and important results which due to space limitation could not be fitted into the paper at last year's conference. (Lord and Koerner, 1986).

In particular, detail is given as to experimental results which allowed us to eliminate certain NDT methods from future considerations. Considerable detail is given as to the ability of the various NDT methods to "pick up" an artificial "Trash Dump". The methods used were metal detection (MD), electromagnetic induction (EMI), magnetometer (MAG) and ground penetrating radar (GPR). The ability of GPR to pick up trench boundaries cannot be over emphasized.

Results concerning the sensitivity of the NDT methods when passing on a scan not directly over the center line of the drums are presented. The GPR response suffers greatly when "off-center". The effect of drum orientation is catastrophic only for GPR; only the horizontal burials are easily picked up. Water table determination with GPR to 16 feet is demonstrated as well as plastic drum detection with EMI. The latter case is an example of void detction.

ACKNOWLEDGEMENTS

We thank the U. S. Environmental Protection Agency for funding of this work through Cooperative Agreement No. CR 807777020. Special thanks are due to Dr. John E. Brugger, the project officer on this Cooperative Agreement, for his constant interest, advice and encouragement. We also wish to thank Ira Wilder, Frank Freestone and Jack Farlow of EPA for their support. A large number of fine Drexel University graduate students deserve credit for their cooperation and enthusiasm in this work.

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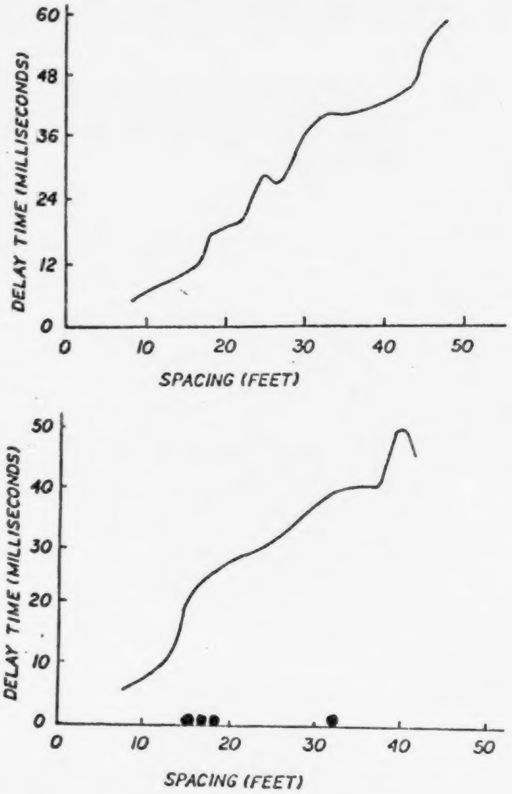


FIG. 1 Seismic refraction survey response; (a) no drums present, (b) four drum pattern present.

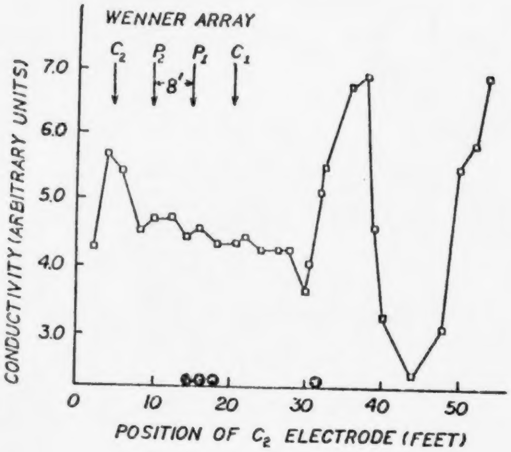


FIG. 2 Electrical resistivity survey response over the four drum pattern.

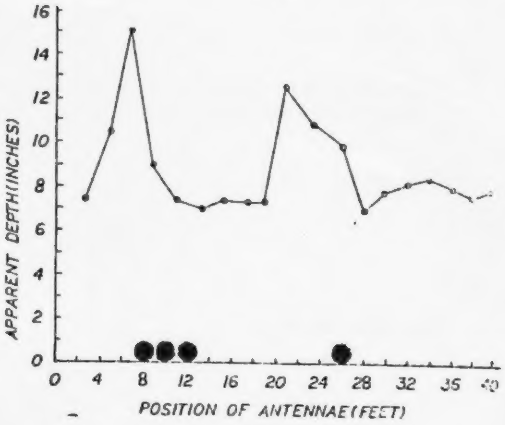


FIG. 3 Continuous wave microwave results for the four drum pattern.

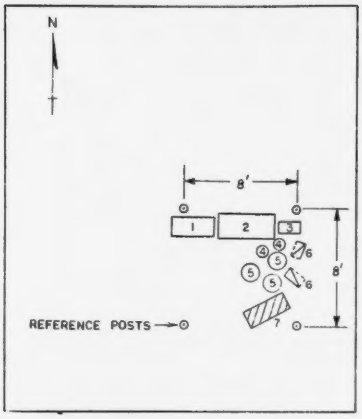

N
8'
1
2
3
4
4
5
5
5
5
6
6
7
8'
REFERENCE POSTS

FIG. 4 Distribution of objects in "trash dump". Key: metal drums: 1: horizontal, 30 gal; 2 horizontal, 55 gal; 3: horizontal, 5 gal; 4: vertical, 5 gal; 5: vertical, 30 gal; 6: 45° angle, 5 gal; plastic drum: 7: horizontal, 30 gal.

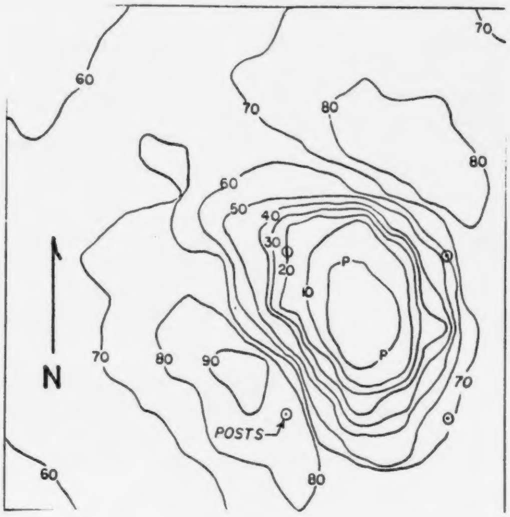

70
60
70
80
80
60
50
40
30
20
10
P
P
N
70
80
90
70
POSTS
60
80

FIG. 6 Electrical conductivity contours in the vicinity of the "trash dump" determined by the EMI technique.

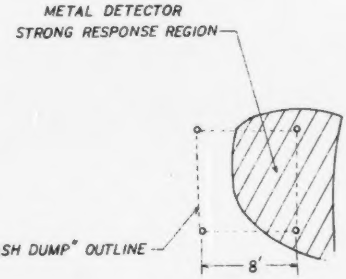

METAL DETECTOR
STRONG RESPONSE REGION
"TRASH DUMP" OUTLINE
8'

FIG. 5 MD response in the vicinity of the "trash dump".

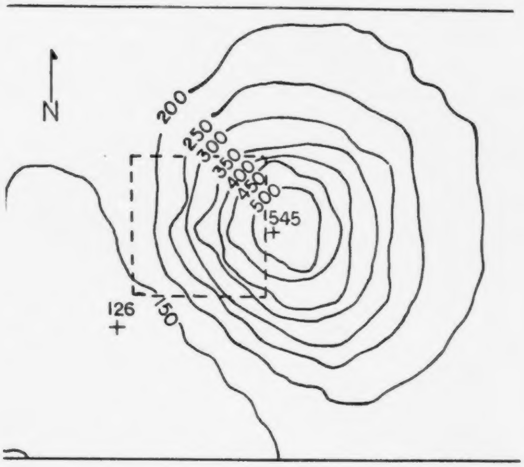

N
200
250
300
350
400
450
500
1545
126
150

FIG. 7 Magnetic field contour map of the "trash dump" using the MAG. The actual magnetic field is 55 x 10^3 γ plus the contour magnetic field label units of γ. The "trash dump" boundary is indicated by the dashed lines.

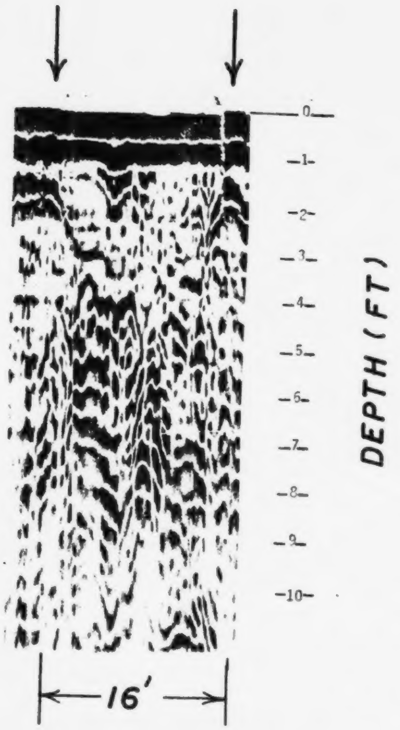
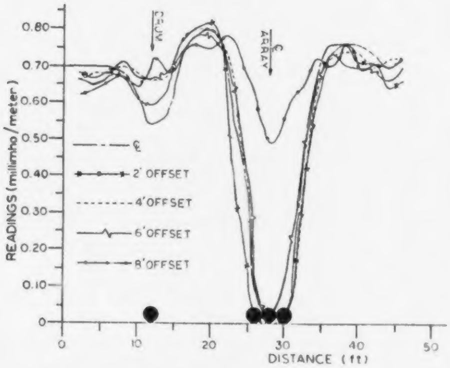
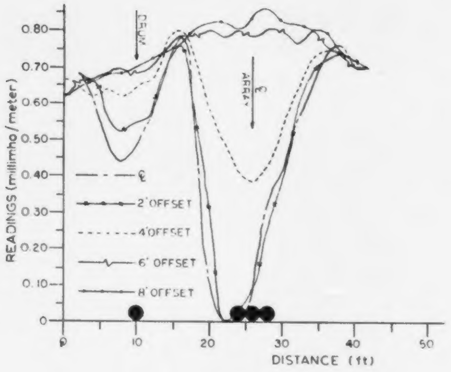


FIG. 8 GPR survey over the "trash dump" showing the excavation boundaries of the burial pit. (Arrows indicate trench boundaries).



9 (a)



9 (b)

FIG. 9 Results of EMI scans over the four 55-gallon steel pattern with various lateral offset (a) antenna ⊥ to scan direction; (b) antenna II to scan direction.

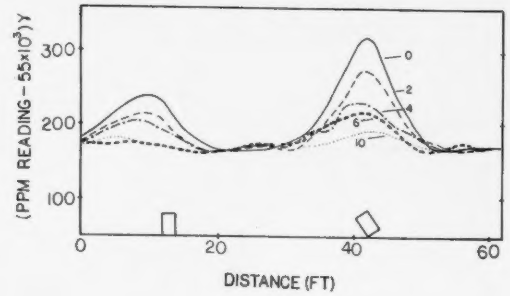


FIG. 10 MAG scans over single steel drums (with about three feet of soil cover) of differing orientations as shown on Figure. Scans at various lateral offsets.

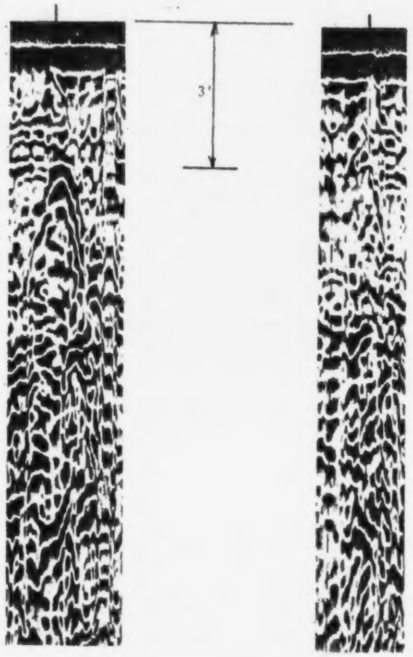
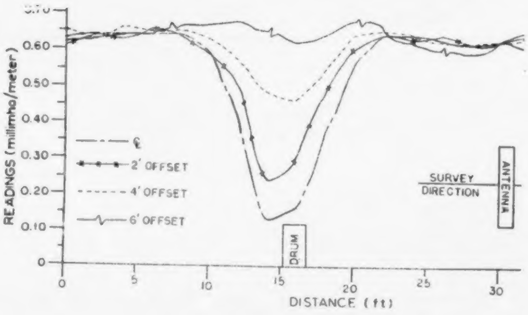
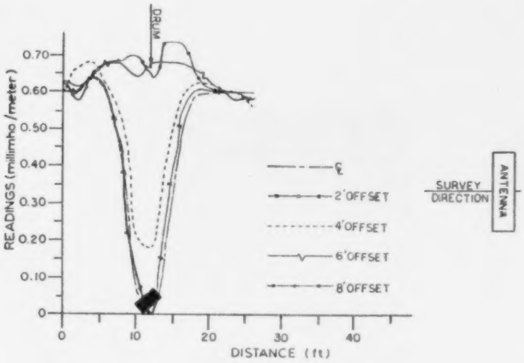


FIG. 11 GPR printouts for a single 55-gallon steel drum buried horizontally with three feet of soil cover. (a) Antenna directly over the drum (b) Antenna displaced two feet from drum centerline.



12 (a)



12 (b)

FIG. 12 EMI scans for 55-gallon steel drums buried with about three feet of soil cover. Drums of various orientations as shown on Figure. Scans at various lateral offsets.

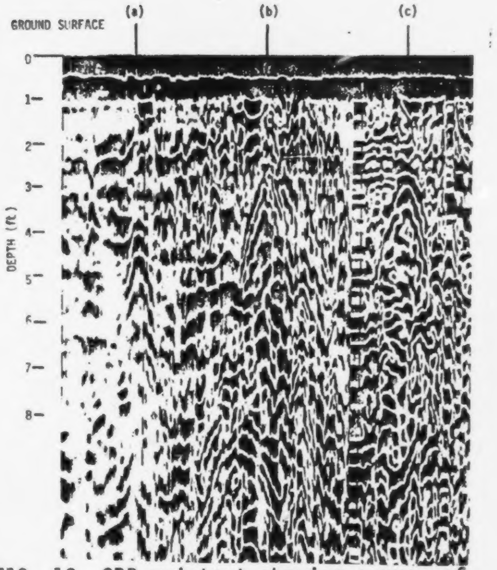


FIG. 13 GPR printout showing survey of 30-gallon steel drums at various orientations buried 3 ft. beneath the surface. (a) Drum standing on end; (b) Drum at 45° angle to ground surface; (c) Drum buried horizontal to ground surface.

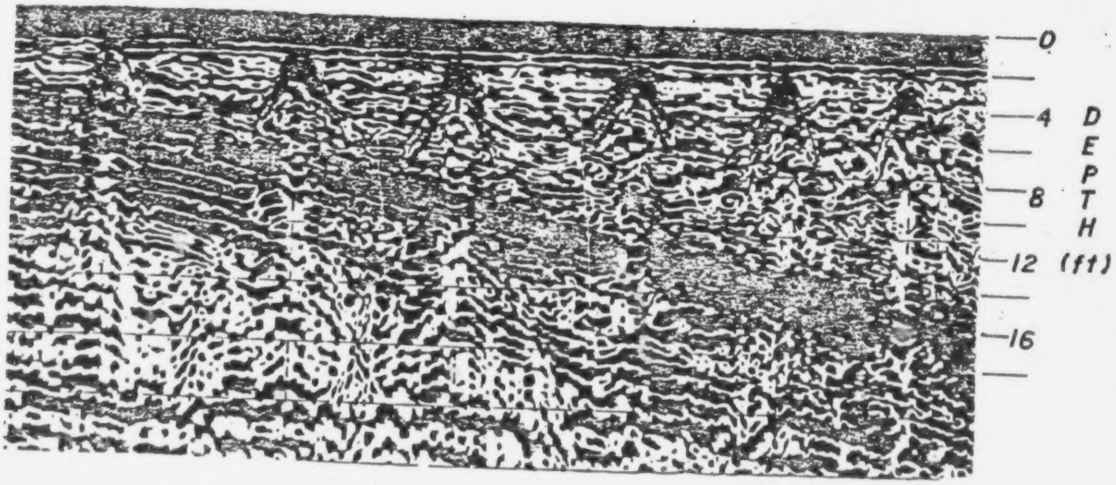


Figure 14 - GPR scans showing the water table, starting at a depth of about 4 feet in the left and going to a depth of about 16 feet at the right (Site 4).

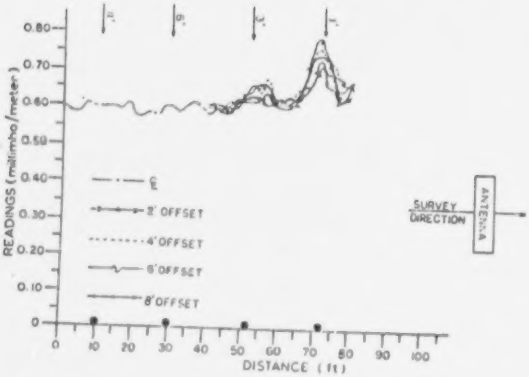


FIG. 15 Results for EMI over empty 40-gallon plastic drums buried with the indicated soil covers. (Site 1).

Table 1. - General Acceptability of Using Various NDT Methods to Locate Typical Sized Buried Containers under Conditions Listed (Maximum Penetration Depth Achieved in Present Studies in (Parentheses)

Steel Containers

Subsurface Material (Reference)	Saturation	Type of Void Water	Metal Detector (MD)	Electromagnetic Induction (EMI)	Ground Penetrating Radar (GPR)	Magnetometer (MAG)
Granular (sand)	0% - 20%	fresh	excellent (6')	excellent (10')	excellent (10')	excellent (10')
	10% - 50%	intermediate	excellent (2')	average (4')	excellent (3')	excellent (4')
	50% - 100%	ocean	not good	not good	poor (2')	excellent (10')
Cohesive (clay)	50% - 100%	fresh	moderate* (4')	moderate* (4')	moderate* (4')	poor (4')**
Water	100%	fresh	excellent (3')	excellent (3')	excellent (4')	excellent (3')
	100%	intermediate	poor	not good	not good	excellent (3')
	100%	ocean	not good	not good	not good	excellent (3')
Plastic Containers						
Granular	10% - 50%	intermediate	not good	not good	excellent - if contents conductive (4'+) fair - if contents non conducting.	not good
	50% - 100%	ocean	not good	not good	poor	not good

*Excellent in dry clay.

**Many interfering magnetic objects. Excellent in absence of interference.

THERMODYNAMIC ANALYSIS OF POST-FLAME REACTIONS APPLIED TO WASTE COMBUSTION

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ABSTRACT

The equilibrium compositions of product gases resulting from the combustion of a few model waste/fuel mixtures have been calculated. These include some chlorinated hydrocarbons (CHCs) and some high nitrogen-containing species. The calculations were carried out with the aid of an interactive, PC-compatible version of a powerful equilibrium solver, STANJAN. Examples are drawn from the more interesting results in order to demonstrate how the theoretical calculations can be interpreted and used to provide insight into the occurrence of products of incomplete combustion (PICs) in incinerator effluents. Practical applications and extensions of the method are also discussed.

INTRODUCTION

It has long been recognized that reaction kinetics, heat and mass transfer are limiting processes to the attainment of chemical equilibrium in combustion processes. Nevertheless, because of the high temperatures and long residence times commonly found in hazardous waste incinerators, there may be situations in which the state of chemical equilibrium is approached, at least on a local basis. In such cases, thermodynamic equilibrium analyses can provide a useful semi-quantitative description of the final system composition. Even when kinetic limitations prevent the attainment of equilibrium, the equilibrium composition of a system is indicative of the state toward which a reacting system is tending. Perhaps most importantly, thermodynamic equilibrium computations provide an overview of system behavior which is not readily apparent in detailed chemical kinetic computations.

There are reasons to believe that the penetration of principal organic hazardous constituents (POHCs) and products of incomplete combustion (PICs) through incinerators has often been associated with some type of non-stoichiometric, fuel-rich condition having occurred within the combustion device. Although the precise reasons leading to a locally fuel-rich stoichiometry have not been fully determined, the occurrence of non-stoichiometric "pockets", "plugs" or "puffs", even with an average condition of excess air, has been suggested (1,2,9,10). For this exploratory study of the post-flame combustion environment (500 K < T < 1500 K), it was assumed that conditions ranged from stoichiometric to fuel-rich. Chemical species examined were primarily hydrocarbons (HC), chlorinated hydrocarbons (CHC), and nitrogen species for which thermodynamic data were readily available. Because of space limitations, only highlights of the investigation are presented in this paper. A preliminary paper containing initial results for CHCs should soon be available (2) and a more complete presentation of results will be available in a future EPA report (3).

METHODS

A powerful, "menu-driven", personal computer (PC) implementation of a code for solving chemical equilibrium problems, STANJAN V3.6, was employed in this research (5). The standard PC version of STANJAN permits the inclusion of up to 20 compounds in an equilibrium computation. By judicious selection, many more than 20 species can be studied under the same specification of temperature and pressure by repeatedly solving the equilibrium problem with new "minor" species. The errors incurred in doing so can be expected to be smaller than the accuracy embodied in the thermodynamic data. The "major" species present at equilibrium were determined by conducting trial computations, including all available compounds, and systematically retaining only those that appeared at high concentrations. It quickly became evident which species needed to be retained for the final computations as whole classes of compounds could be ignored for the cases studied, e.g., alkanes.

Thermochemical data on entropy and enthalpy functions were prepared in a form suitable for use with STANJAN. The chemical species used in the calculations are shown in Table 1 along with the source of the data. The data were used without further critical evaluation. In some cases the thermodynamic functions were only available to 1000 K and a smoothing algorithm in the STANJAN package was used to extend the data to 6000 K as required by STANJAN. Since only the lower temperature range (T < 1500 K) was of interest, extrapolation errors probably do not have a significant effect upon the predicted equilibrium concentrations, as many compounds occur at negligible concentrations in the temperature range above 1000 K.

For all the cases examined, equivalence ratio (E.R. = $[\text{fuel/air}]_{\text{actual}}/[\text{fuel/air}]_{\text{stoichiometric}}$) was varied from 1.0 (stoichiometric) to 2.0 (highly fuel-rich). For the CHC computations, hydrogen-to-chlorine ratio was also varied from 1:3 to 3:1. Although the lower H:Cl ratio would be unrealistic in an "average" sense, it is conceivable that incomplete blending of the waste/fuel mixture could lead to introduction of short-term fluctuations in composition that could approach or even be less than 1:3, e.g., tetrachloroethene (specific gravity = 1.6) that may have stratified in a tank. Furthermore, in some cases the fuel and the waste are introduced into the combustion unit as separate streams, again resulting in the possibility of low H:Cl, on a local basis, caused by inadequate mixing. As will become evident from the computational results, it would not require large amounts of an inadequately blended feedstock or poorly mixed gases to result in emission levels comparable to those seen in field tests.

The predicted equilibrium concentrations are only meaningful in the sense that the "correct" chemical species have been included in the computation. Thus, if a major specie which would form at equilibrium, such as CO, were to be left out of a computation, the results would be in serious error. Lack of thermodynamic data prevented a full study of all chlorinated ethenes and benzenes. Thus some species that have been observed in source tests and which may have measurable concentrations, e.g., a mole fraction greater than about 1 E-10 (0.1 ppb), have been ignored. The figures presented in the results show concentrations only of those species of particular interest.

Some compounds were predicted to reach significant concentrations, but only at the lower extreme of the temperature range ($T < 750$ K), e.g., graphitic carbon, C(s). Under such conditions, kinetic limitations exist which prevent that condition from becoming an accessible thermodynamic state. In such cases, the computations were repeated, removing the "offending species" to determine the "next" thermodynamically favored compound. The validity of such manipulations is questionable, nevertheless, insight regarding alternative reactions of possible importance can be obtained using such a procedure, e.g., benzene, chlorinated benzenes and dioxins became significant species in some cases when formation of C(s) was eliminated.

It is well known that molecular nitrogen, N_2, present in the combustion air is not particularly reactive. Therefore, only the nitrogen that was assumed to be present in the waste molecules was allowed to be "reactive". A pseudo-species having the thermal properties of molecular nitrogen was included in the equilibrium calculations to achieve the composition of reaction products that would correspond to combustion with air. The system compositions were varied in accordance with the type of waste assumed, e.g., hydrogen cyanide, acetonitrile or acrylonitrile. Equivalence ratios were varied as described above. No attempt was made to undertake a systematic survey of nitrogen-chlorine interactions, e.g., nitrosyl chloride formation.

SELECTED RESULTS AND DISCUSSION

The most striking results of the equilibrium calculations occurred for simultaneous conditions of fuel-rich stoichiometry, E.R. > 1.0, and an H:Cl ratio ≤ 1.0. An example of the results is shown in Figures 1a, 1b and 1c for a system composition 1C:1H:3Cl (H:Cl = 0.33) and equivalence ratios of 1.0 (stoichiometric), 1.01 (1% oxygen deficiency), 1.05 (5% oxygen deficiency). Note that at lower temperatures, under even the slightest fuel-rich conditions, CCl_4 and $COCl_2$ became major thermodynamically stable species. The temperature region over which their concentration increased rapidly began at about 1000 K (about 700°C). This is probably a sufficiently high temperature for the system to tend toward the equilibrium state given typical post-flame residence times of about two seconds, and the relatively low bond strength of Cl_2 molecules (239 kJ/mole). However, detailed kinetic calculations or experiments would be needed to confirm these predictions. Certainly for temperatures below 500 K, reactions would have slowed dramatically and the predicted equilibrium states would not be attained.

Several additional observations were noteworthy in the CHC calculations.

1. There was a competition among Cl and O ("oxidizing" species) for the C and H (more-or-less chemically "reducing" species in the systems examined). Formation of CO_2, H_2O and HCl was essentially quantitative under stoichiometric or fuel-lean conditions.

2. Under fuel-rich conditions, as the H:Cl ratio decreased, increasingly chlorinated methanes were observed as stable products in the lower temperature range < 1000 K, i.e., chloromethane ---> tetrachloromethane.

3. Under slightly fuel-rich conditions ($1.0 <$ E.R. < 1.05), solid carbon, benzene, chlorinated benzenes and chlorinated dioxins were each predicted to form at low temperatures. Solid carbon and benzene were thermodynamically favored products with an excess of hydrogen present, while solid carbon, chlorinated dioxins and chlorinated benzenes were favored products for an H:Cl ratio of 1.0. When the H:Cl ratio was less than 1.0, none of the above species were predicted to form because the Cl would directly oxidize the C atoms to produce primarily chlorinated methanes (especially CCl_4).

4. Recognizing that kinetic limitations would prevent the attainment of the equilibrium predictions described in (3) above, the occurrence of solid carbon, benzene, chlorinated benzenes and chlorinated dioxins was successively eliminated. For H:Cl > 1.0, when solid carbon was disallowed, the tendency was to form benzene, then ethylene and chloromethane (Figures 2a, 2b,

2c). For H:Cl = 1.0, and a fuel-rich stoichiometry, E.R. = 2.0 the corresponding tendency was to form solid carbon, chlorinated dioxins, chlorinated benzenes, benzene, chlorinated methanes (Figures 3a,3b,3c,3d, 3e,3f).

One inference that can be drawn from the tendencies described above is that it is quite likely that trace amounts of the above species could be formed in the cooling combustion gases if the composition of the system corresponded to those assumed. One can also speculate that chemically simpler species, e.g., chlorinated methanes and ethenes, would be more likely to be formed at detectable concentrations than those which require a longer sequence of elementary reaction steps, i.e., chlorinated methanes > benzene, ethylene, or chlorinated ethenes and benzenes > chlorinated dioxins. For the most part, it is the authors' belief that this is consonant with observed test results obtained from incinerators that most closely correspond to the equilibrium assumptions, e.g., mineral kilns and circulating bed combustors. In these types of devices, strong transverse turbulent mixing may actually impede longitudinal mixing, leading to a condition approximating "plug-flow". As a practical application of these insights, it can be suggested that it would be prudent to insure adequate blending of waste streams with an excess of hydrogen (in the fuel) and adequate mixing of the combustion gases in a temporal sense, i.e., the mixing process should produce both good microscale mixing and avoidance of non-stoichiometric "puffs" or plugs". Otherwise, high temperature alone will not guarantee low emission levels because some CHCs can simply re-form upon cooling.

The initial exploration of the nitrogen compounds under fuel-rich conditions has not led to any remarkable insights, other than that molecular nitrogen in the combustion air should not be included as a reactant in the system. If a diluent gas having the properties of N_2 was not substituted for the N_2 in the combustion air, then unrealistically large amounts of HCN (hydrogen cyanide), C_2H_3N (acetonitrile) and C_3H_3N (acrylonitrile) were predicted to be present as stable combustion products. Otherwise, the principal nitrogen-containing species observed was ammonia with only trace levels of HCN, C_2H_3N, and C_3H_3N. Some typical results for the "pseudo-nitrogen" computations are shown in Figures 4a, 4b and 4c.

CONCLUSIONS

This exploratory study has shown that some valuable insights regarding combustion processes can be obtained from thermodynamic equilibrium analyses. A wealth of thermodynamic data exists for use with a very convenient computational tool, STANJAN. Besides the CHCs and nitrogen compounds, data are available for fluorine, sulfur and metals. A systematic study of trace species of environmental concern may prove to be valuable, not only for hazardous waste incineration but for other types of thermal processes as well.

A summary of specific findings is given below:

1. CHCs are thermodynamically stable compounds under fuel-rich conditions, with low H:Cl ratios a condition to be particularly avoided. Trace levels of such species can persist in the combustion effluent even if only a small fraction of the waste encounters the conditions described above. Such conditions can arise from inadequate blending of fuel/waste mixtures and incomplete mixing with combustion air before leaving the high temperature zone of an incinerator.

2. In real systems CO would be expected under the fuel-rich conditions. There are reasons why CO levels might increase without a concommitant increase in CHC emissions. However, it appears unlikely that high levels of CHC emissions are possible without at least a moderate increase in CO levels.

3. Thermodynamic analyses may be useful in identifying species for which sampling methods need to be developed. As an example, $COCl_2$ (phosgene) is predicted to be present at trace levels when compounds such as CCl_4 (carbon tetrachloride) are present in the

combustion effluent. Because $COCl_2$ is a gas at ambient temperatures and readily hydrolyzed, its presence may have gone undetected using current sampling methods.

4. The initial screening of nitrogen-containing wastes did not identify any major potential problems with residual emissions under fuel-rich conditions, under the assumption that N_2 in air was not available for reaction.

5. Additional kinetic studies are needed to determine the range of applicability of the thermodynamic predictions. At present, it can only be said that the predictions are in qualitative agreement with field and laboratory tests where the equilibrium assumptions were most closely satisfied.

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Erratum:

In the set of calculations for H:Cl = 3:1 (fuel equivalent to CH_3Cl), methane (CH_4) was inadvertently left out under fuel-rich conditions. As a result C(s) was predicted to be the major thermodynamically stable species at low temperatures (Figure 2a). When CH_4 is included, it becomes the major species and C(s) disappears as a stable phase. Figures 2a, b and c therefore represent the predicted system compositions if CH_4 (Figure 2a), C(s) (Figure 2b), and C_6H_6 (Figure 2c) are successively removed from the system. The major conclusions of the study remain unchanged.

TABLE 1. LISTING OF CHEMICAL SPECIES STUDIED

Species	Composition	Reference
Organics:		
methane	CH_4	7
acetylene	C_2H_2	4
ethylene	C_2H_4	4
benzene	C_6H_6	4
toluene	C_7H_8	4
styrene	C_8H_8	8
naphthalene	$C_{10}H_8$	8
dibenzo-p-dioxin	$C_{12}H_8O_2$	6
biphenyl	$C_{12}H_{10}$	8
anthracene	$C_{14}H_{10}$	6
Chlorine Containing Species:		
tetrachloromethane (carbon tetrachloride)	CCl_4	7
trichloromethane (chloroform)	$CHCl_3$	7
dichloromethane (methylene chloride)	CH_2Cl_2	7
chloromethane	CH_3Cl	7
carbonyl dichloride (phosgene)	$COCl_2$	7
dichloroacetylene	C_2Cl_2	7
tetrachloroethene (perchloroethylene)	C_2Cl_4	7
hexachloroethane	C_2Cl_6	7
trichloroethene (trichloroethylene)	C_2HCl_3	8
pentachloroethane	C_2HCl_5	8
1,1-dichloroethene (dichloroethylene)	1,1-$C_2H_2Cl_2$	8
1,2-dichloroethene (dichloroethylene)	1,2-$C_2H_2Cl_2$	8
chloroethene (vinyl chloride)	C_2H_3Cl	8
1,1,2-trichloroethane	1,1,2-$C_2H_3Cl_3$	8
1,1-dichloroethane	1,1-$C_2H_4Cl_2$	8
1,2-dichloroethane	1,2-$C_2H_4Cl_2$	8
hexachlorobenzene	C_6Cl_6	8
1,2,3-trichlorobenzene	1,2,3-$C_6H_3Cl_3$	6
meta-dichlorobenzene	2,4-$C_6H_4Cl_2$	8
chlorobenzene	C_6H_5Cl	8
monochlorodibenzo-p-dioxin (MCDD)	$C_{12}H_7O_2Cl$	6
tetrachlorodibenzo-p-dioxin (TCDD)	$C_{12}H_4O_2Cl_4$	6
octachlorodibenzo-p-dioxin (OCDD)	$C_{12}O_2Cl_8$	6
chlorine, atomic	Cl	6
chlorine, molecular	Cl_2	7
hydrogen chloride	HCl	7
Nitrogen Containing Species:		
methylamine	CH_5N	8
acetonitrile	C_2H_3N	8
ethylenimine	C_2H_5N	8
ethylamine	C_2H_7N	8
acrylonitrile	C_3H_3N	8
pyrrolidine	C_4H_9N	8
pyridine	C_5H_5N	8
aniline	C_6H_7N	8
benzonitrile	C_7H_5N	8
hydrocyanic acid (cyanide)	HCN	7
nitroxyl hydride (nitrosyl hydride)	HNO	7
nitrous acid	HNO_2	7
nitric acid	HNO_3	7
nitrogen, atomic	N	7
ammonia	NH3	7
nitrogen monoxide (nitric oxide)	NO	7
nitrogen dioxide	NO_2	7
nitrogen trioxide	NO_3	7
nitrogen, molecular	N_2	7
dinitrogen monoxide (nitrous oxide)	N_2O	7
Additional Inorganic Species:		
carbon monoxide	CO	7
carbon dioxide	CO_2	7
dihydrogen monoxide (water)	H_2O	7
oxygen, atomic	O	7
oxygen, molecular	O_2	7

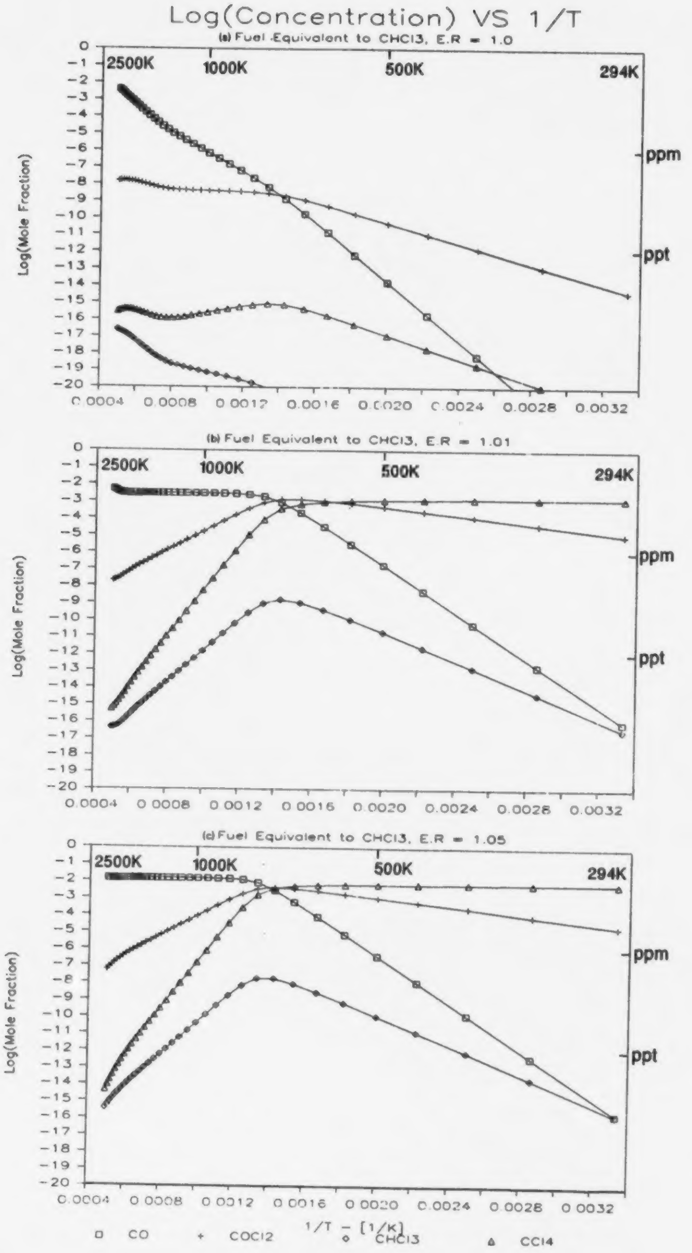

Figure 1. Composition versus inverse temperature for a system equivalent to $CHCl_3$ fuel (chloroform) burned with air under (a) stoichiometric conditions, (b) 1% oxygen deficiency (c) 5% oxygen deficiency. Symbols spaced every 50K.

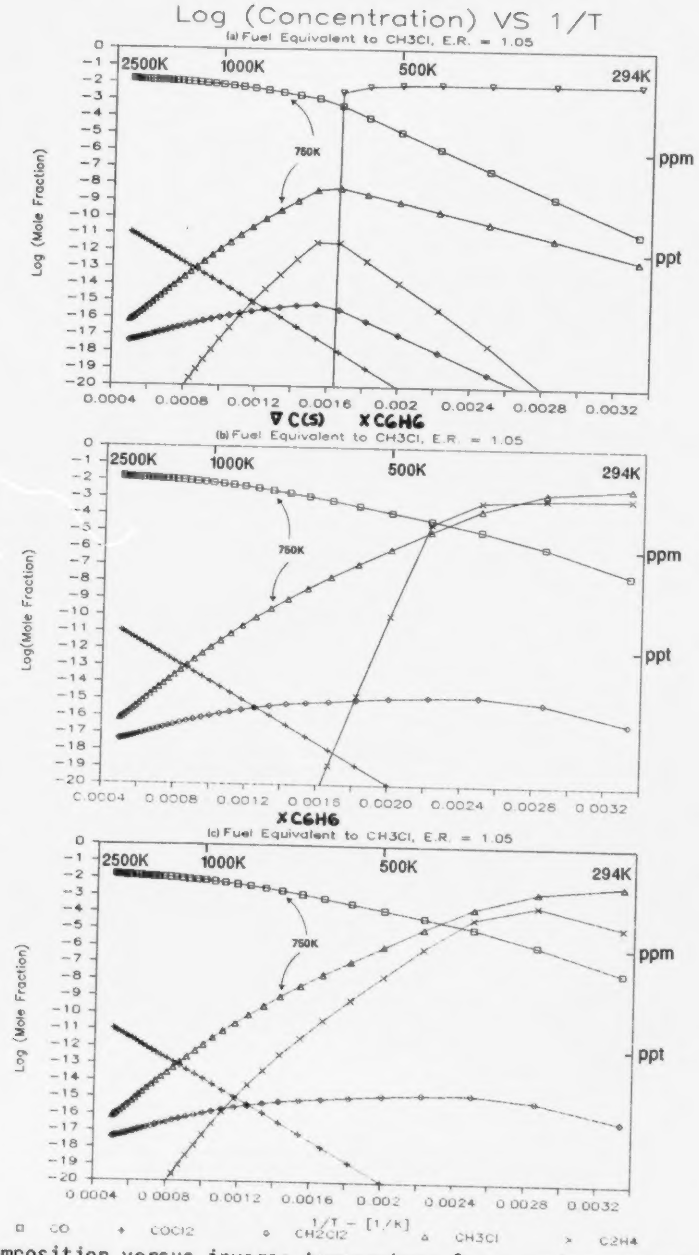

Figure 2. Composition versus inverse temperature for a system equivalent to a CH_3Cl fuel (chloromethane) burned with air at E.R. = 1.05 (slightly fuel-rich): (a) allowing C(s) as a reaction product (b) disallowing C(s) (c) disallowing both C(s) and C_6H_6 as reaction products. In reality, the same levels of CH_3Cl are predicted, order of ppb, since reaction kinetics slow dramatically below 750K.

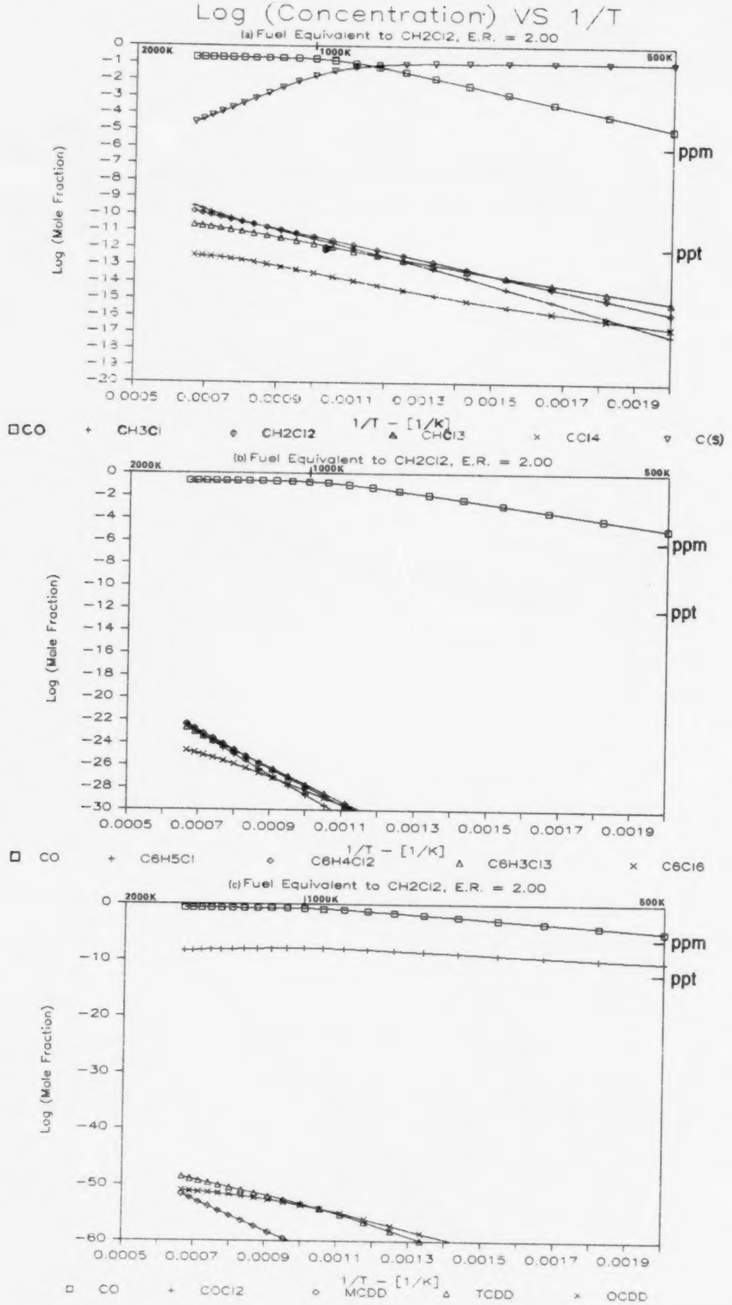

Figure 3. Composition versus inverse temperature for a system equivalent to CH_2Cl_2 fuel (dichloromethane) burned with air under a fuel-rich condition (E.R. = 2.0): (a), (b), (c) present calculations including the presence of C(s).

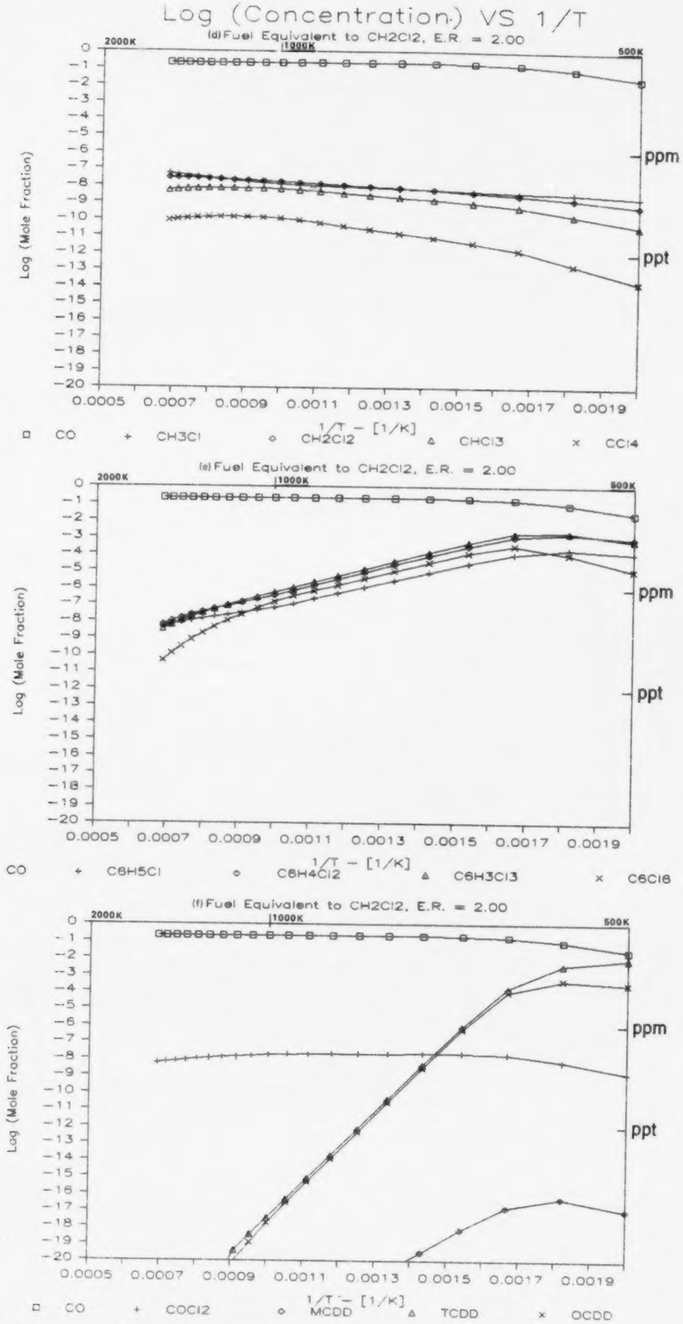

Figure 3. Continued - Composition versus inverse temperature for a system equivalent to CH_2Cl_2 fuel (dichloromethane) burned with air under a fuel-rich condition (E.R. = 2.0): (d), (e), (f) present the same system, but excluding C(s).

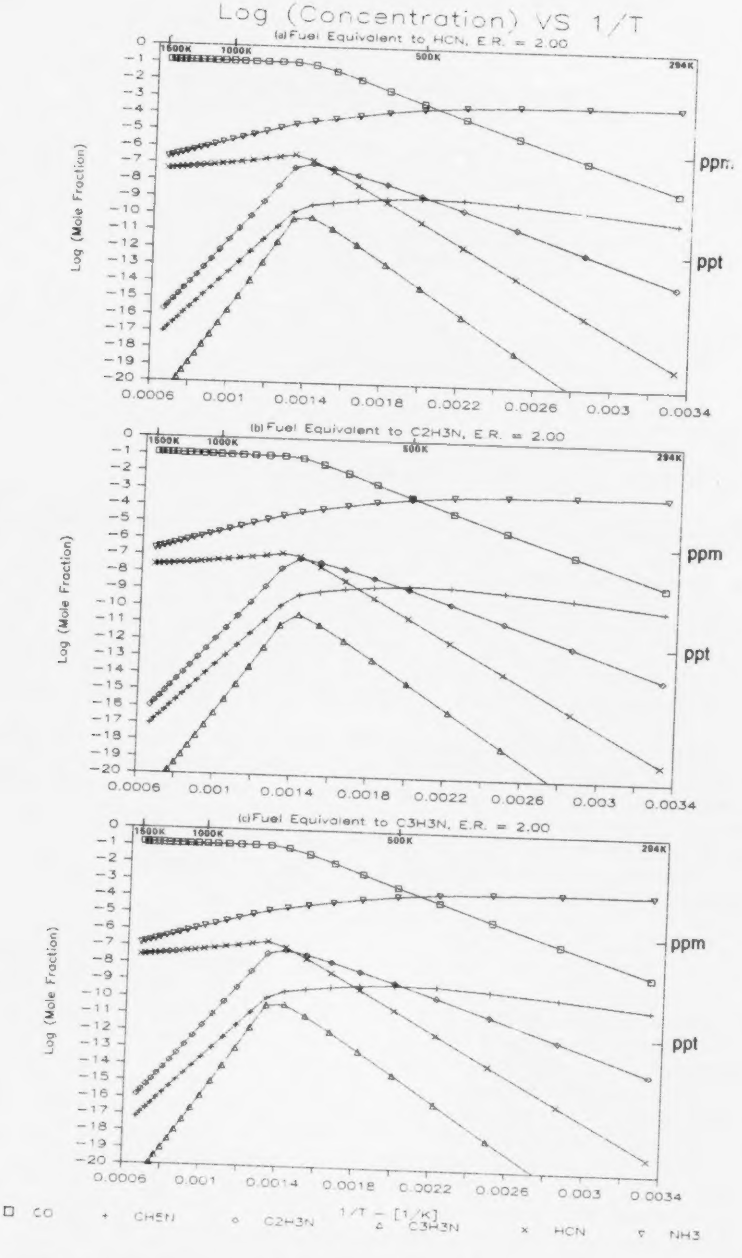

Figure 4. Composition versus inverse temperature for nitrogen based fuels, E.R. = 2.0: (a) fuel equivalent to HCN (hydrogen cyanide) (b) fuel equivalent to C_2H_3N (acetonitrile) (c) fuel equivalent to C_3H_3N (acrylonitrile).

INFLUENCE OF ATOMIZATION PARAMETERS ON DROPLET STREAM TRAJECTORY AND INCINERATION

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ABSTRACT

In the incineration of liquid hazardous wastes, atomization quality may limit destruction efficiency. Large, non-mean droplets in a fuel spray can pass through the flame zone prior to complete evaporation, and may subsequently fail to burn completely due to insufficient temperature and/or flame radicals. A study is ongoing to develop a predictive understanding of individual droplet trajectories in turbulent diffusion flames. Experiments in a cold quiescent flow environment, a laminar flow flat-flame burner, and a 100 kW swirling, turbulent combustor have been conducted to calibrate a model to predict three-dimensional trajectories of single monodisperse droplet streams.

Escape from the flame zone of large (> 200 μm diameter) fuel oil/xylene droplets has been observed as a function of initial droplet size, velocity, spacing, and injection angle. Incomplete incineration of these droplets was found to be related strongly to droplet penetration of the flame zone. Minimum model requirements to successfully predict droplet trajectories in turbulent diffusion flames include: droplet spacing effects on drag; droplet/droplet interaction effects on evaporation; evaporation effects on drag; and turbulence effects on droplet ballistics.

INTRODUCTION

Of the hazardous organic wastes produced in the U.S., about 75 percent are liquids or dissolved in liquids. With landfill disposal of these wastes becoming increasingly unacceptable due to growing public concern and increased levels of hazardous waste production, thermal destruction is being considered as an alternative disposal method. Successful incineration requires that flame radicals and high temperatures be combined in such a way that the principal organic hazardous components (POHCs) of the feed waste are destroyed and that the formation of products of incomplete combustion (PICs), which may be as hazardous as, or even more hazardous than, the original POHCs, are minimized. Proper spray atomization provides the necessary dispersion of liquid fuel and waste into the oxidizer to avoid incinerator failure by inadequate mixing. Fuel spray nozzles degrade with use and must be replaced periodically. Therefore, there is a need to understand and quantify how atomization parameters limit liquid waste incineration so that a sound rationale for selecting and replacing spray nozzles can be defined.

Four group combustion modes of a fuel droplet cloud have been identified [1], with single droplet combustion being applicable in practice to only a very limited number of special situations. Such a special situation, however, can arise during the incineration of liquid hazardous wastes, where droplets with large diameters (as much as an order of magnitude larger than the mean) congregate at the outer edge of fuel spray cones [2]. One or more of these large, errant droplets may individually pass through, or bypass, the main flame zone and lead to a failure mode in the incinerator. For example, bypassing of as few as 1 drop out of 10 million drops can lead to failure to meet a destruction removal efficiency (DRE) in excess of 99.99 percent, as is required by law.

Motivation for the current study lay, therefore, in the need to predict single, non-mean droplet trajectories in a turbulent flame zone. To this end, experiments have been conducted (1) to determine minimum requirements of a model that successfully predicts measured trajectories of single monodisperse droplet streams in three-dimensional turbulent diffusion flames, and (2) to relate droplet penetration of the flame zone to potential incinerator failure modes.

THEORY

A semi-empirical numerical model is being developed for predicting the ballistics of burning droplet streams in turbulent diffusion flames. An important input to this model is a proper representation of the drag coefficient on a non-evaporating droplet in a stream.

Drag Coefficient

While much information is available on the relationship of the drag coefficient, C_D, of an isolated sphere to Reynolds number, Re, little is available on the dependence of C_D on Re and droplet spacing, non-dimensionalized by droplet diameter, D, as L/D. As droplet spacing is reduced, drag is reduced due to wake effects. For large droplet spacings, when droplets cease to interact, the drag coefficient, C_D^{∞}, for each one is that of an isolated sphere, and is only a function of Re. For the slightly distorted droplets formed by a vibrating capillary droplet generator, the relation of Lambiris and Combs [3] is recommended:

$$
\begin{aligned}
C_D^{\infty}(\mathrm{Re}) &= 27\,\mathrm{Re}^{-0.84} &&;\ 0 < \mathrm{Re} < 80 \\
&= 0.27\,\mathrm{Re}^{0.217} &&;\ 80 < \mathrm{Re} < 10^4 \qquad (1) \\
&= 2 &&,\ \mathrm{Re} > 10^4
\end{aligned}
$$

In the other extreme, as droplet spacing approaches the droplet diameter, the drag coefficient may be assumed to approach the friction drag coefficient of a long rod, which can be calculated from the theory of Glauert and Lighthill [4]. A general form for the asymptotic form for the drag coefficient, C_D°, of a sphere as L/D approaches unity is obtained by a Taylor expansion about L/D = 1; thus, C_D° is hypothesized to be:

$$C_D^{\circ}(\mathrm{Re},L/D) = 0.755/\mathrm{Re} + a\mathrm{Re}^b\,[L/D-1] \qquad (2)$$

where a and b are parameters to be determined from experiment. The factor $[a\mathrm{Re}^b]$ multiplying [L/D-1] is hypothesized to be a function of Reynolds number, since the extent of droplet interaction as L/D approaches 1 will depend on Re, the latter quantity determining the length of wake behind each droplet [5]. An effective and universal technique to correlate data, obtained between regions of validity for the asymptotic forms for C_D as L/D --> 1 and L/D --> ∞, is to use the asymptotic expansion formula developed by Churchill [6]:

$$
\begin{aligned}
&[C_D(\mathrm{Re},L/D)]^{-n} = \\
&\qquad [C_D^{\circ}(\mathrm{Re},L/D)]^{-n} + [C_D^{\infty}(\mathrm{Re})]^{-n} \qquad (3)
\end{aligned}
$$

where n is a parameter to be obtained by experiment.

Trajectory Model

A simple, numerical model has been developed for predicting the ballistics of an isolated burning droplet [7]. The model is being refined to include effects of droplet interaction on drag and evaporation rate, evaporation effects on drag, and turbulence effects on droplet ballistics. The model is used to solve the uncoupled equations of droplet motion in a Lagrangian framework. A three-dimensional grid structure is established for specifying the background gas velocity (v_g), temperature (T_g), and chemical speciation. Calculations are terminated when the droplet exits the computational domain.

Drag and gravitational forces are assumed to be the only external forces on the droplet. The drag force, F_D, has two vector components (F_{D1} and F_{D2}). The drag coefficient with droplet spacing effects (C_D) is applied to the drag component in the droplet stream direction; the drag coefficient without spacing effects (C_D^∞) is applied to the other drag component. F_{D1} is defined to be aligned with the droplet velocity vector, v_d; F_{D2} is then perpendicular to the plane containing v_g and v_d (Fig. 1). The magnitudes of the force vectors are given by:

$$\begin{aligned} |F_{D1}| &= C_D{}^* \frac{\rho_a A}{2} v_{r1} \\ |F_{D2}| &= C_D^\infty{}^* \frac{\rho_a A}{2} v_{r2} \end{aligned} \tag{4}$$

where v_{r1} is the component of relative velocity ($v_r = v_d - v_g$) aligned with v_d and $v_{r2} = v_r - v_{r1}$. The evaporating droplet drag coefficient (* denotes mass transfer) has been determined by Eisenklam, et al. [8]. Evaporation has been found to decrease drag by a factor η_e ($\eta_e = C_D{}^*/C_D$), given by:

$$\eta_e = 1/(1 + B) \tag{5}$$

where B is the mass transfer number, defined by equation 8c. Force balance yields:

$$\begin{aligned} \Sigma F_x &= ma_x = F_{D1x} + F_{D2x} \\ \Sigma F_y &= ma_y = F_{D1y} + F_{D2y} + F_{grav} \\ \Sigma F_z &= ma_z = F_{D1z} + F_{D2z} \end{aligned} \tag{6}$$

where F_{grav} is the gravitational force ($= -mg$).

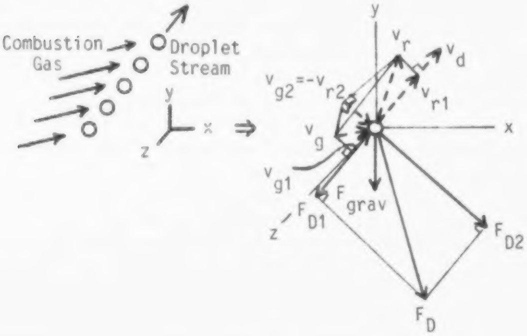


Figure 1. Vector diagram in three dimensions. Velocities shown with dotted lines; forces shown with solid lines.

Heat and mass transfer are modeled in two steps: droplet heating to the liquid boiling point, followed by droplet evaporation. During droplet heating, its diameter is assumed to be constant (i.e., no evaporation), and its temperature (T) is assumed to be uniform (i.e., low Biot number). Here, the time rate of change of the droplet temperature is given by:

$$\frac{dT}{dt} = 6 \frac{Nu\ k_g}{D^2 c_{p\ell} \rho_\ell} [T^\infty - T] \tag{7}$$

where the Nusselt number (Nu) is calculated using an empirical relation. After the droplet temperature reaches the boiling point, evaporation begins. In this stage, the time rate of change of the droplet diameter is given by:

$$\frac{dD}{dt} = -C_B \frac{1}{2D} [1 + 0.23\ Re^{0.5}]\ \eta_s \tag{8a}$$

where the evaporation constant (C_B) is given by:

$$C_B = \frac{8\ k_g}{\rho_\ell c_{p\ell}} \ln (1+B) \tag{8b}$$

and where the mass transfer number (B) is given by:

$$B = \frac{c_{p\ell}\ (T^\infty - T)}{L} + \frac{Q\ Y_{O\infty}}{\sigma\ L} \tag{8c}$$

Here, k_g, ρ_ℓ, and $c_{p\ell}$ are properties of the liquid and background gas, Q is the heat of combustion of the droplet, L is the latent heat of vaporization, $Y_{O\infty}$ is the mass fraction of the oxidizer in the background gas, and σ is the oxidizer-to-fuel mass ratio. The effect of multiple droplet interaction on evaporation rate, accounted for by η_s, has been quantified by Labowsky [9]:

$$\eta_s = 1 - (2L/D)^{-1} + (2L/D)^{-2} \tag{9}$$

Turbulence effects on droplet dispersion are modeled via the stochastic approach proposed by Dukowicz [10]. By this "discrete droplet" method the gas turbulence is randomly sampled during each droplet's flight and allowed to influence its motion. The total stream behavior is obtained by averaging over a large number of droplets. The number of droplet paths simulated is determined statistically, with the number being sufficient to describe a distribution of trajectory endpoints.

EXPERIMENTAL METHODS

The objectives of this study are: (1) to measure and predict the three-dimensional trajectories of single monodisperse droplet streams in turbulent diffusion flames, and (2) to study the relation of these trajectories with droplet incineration effectiveness.

The 100 kW combustor, modified for simulation of flame aerodynamics at the expense of time/temperature simulation, and monodisperse droplet generator (Fig. 2) have been described previously [11]. Firing natural gas, two flame shapes with very different mixing patterns were established: Types C and A. The short, swirling Type C flame is stabilized by strong internal recirculation, whereas the long, axial Type A flame is stabilized by external recirculation. Radial profiles of temperature, velocity (three components), and species were measured. Gas temperatures were measured by suction pyrometry; axial, radial, and tangential velocity components were measured by using a specially designed five-hole pitot probe (water-cooled with 0.8 cm uncooled tip, calibrated). "Instantaneous" velocities of the turbulent flow were recorded, with means and standard deviations calculated by microcomputer. Measured radial profiles of axial velocity were consistent with overall mass balance.

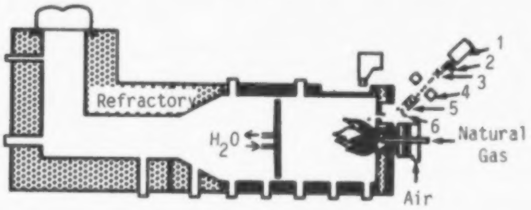


Figure 2. Turbulent diffusion flame modular combustion facility. A 50 cm internal diameter, 90 cm long near-burner combustion module is water-cooled and insulated with a 4 cm thick refractory lining. An International Flame Research Foundation burner has a movable-block air swirl generator and interchangeable fuel nozzles. A monodisperse droplet generator is equipped with electronics for droplet separation. It consists of a vibrator (1), liquid supply (2), orifice (3), pulsed charging ring (4), deflection plates (5), and trap (6). A water-cooled coil allows for quenching the combustion gases at variable axial locations.

The droplet generator is a vibrating orifice device with ancillary electronics to facilitate droplet spacing variation. Initial droplet diameter and spacing were measured via strobe photography. Initial droplet velocity was calculated from the vibrator frequency setting. The fluid tested, chosen on the basis of conductivity (for electrostatic charging and deflection) and viscosity (for droplet formation), was a mixture of 80 percent (by volume) Shell Oil Company fuel additive ASA-3, comprised mostly of xylene (C_8H_{10}), and 20 percent distillate fuel oil.

Droplet trajectories were measured with the aid of high speed photography. Droplet destruction efficiency was determined by measuring the increased levels of exhaust unburned hydrocarbons (UHC, or surrogate POHC) and carbon monoxide (CO, or PIC) due to droplet injection. These emission measurements were taken from the stack where the combustion gases are well mixed. Flame ionization was used to detect UHC, and an infrared instrument was used for CO measurement. A removable water-cooled coil for quenching the combustion gases was inserted, resulting in a bulk gas residence time of 0.6 s before quenching.

To determine droplet spacing effects on the non-evaporating droplet drag coefficient, trajectory experiments were conducted in the cold flow, quiescent environment within an observation tunnel. Empirical parameters a, b, and n (equations 2 and 3) were evaluated. Two-dimensional laminar flow experiments in a bench-scale flat-flame burner were then conducted to calibrate the model, allowing minimum model requirements to be determined without the complexities of three dimensions and turbulence. In the 100 kW turbulent diffusion flame experiments, baseline measurements (i.e., without droplet injection) of combustion gas temperature and velocity were taken. Droplet trajectories were observed for a variety of initial droplet stream conditions, including variation in droplet size, velocity, spacing, and injection angle. Finally, droplet incineration was measured with the quench coil inserted.

COLD FLOW TRAJECTORIES

Parameters a, b, and n were estimated using data from 10 full trajectories. Nonlinear regression for parameter estimation was accomplished using a modified Marquardt [12] algorithm, which is based on a multidimensional search in parameter space for the minimum value of a sum of squares functional measuring deviation from the data. The least squares parameter estimates were: $a = 34.8$, $b = -1.009$, and $n = 0.7072$.

Measured and predicted trajectory endpoints are shown in Fig. 3 for the 10 trajectories in regression and for 39 additional trajectories. More detailed results from the experiments will be published in a separate paper.

LAMINAR FLOW EXPERIMENTS

Trajectories of non-burning and burning droplets in a flat-flame burner were measured to test the model in this aerodynamically simple environment. These results, shown in Fig. 4, demonstrate that droplet interaction effects on evaporation rate and evaporation effects on drag are important model requirements. Droplet interaction can reduce the evaporation rate by up to 25 percent ($n_s = 0.75$); evaporation can reduce drag by as much as 70 percent ($n_e = 0.30$).

TURBULENT DIFFUSION FLAME TRAJECTORIES

In baseline tests without droplet injection the combustion gas flow field was characterized in terms of temperature and velocity. A peak temperature of 1750 K was measured at the combustor centerline, decreasing to 1100 K near the wall. Axial, radial, and tangential velocity components were measured, with a peak total velocity of 26 m/s measured near the burner quarl exit. The standard deviation of velocity measurement often exceeded 50 percent of the mean velocity. Axial symmetry was observed, both in temperature and velocity. (See reference 11 for more details.) These results were then used as inputs to the trajectory model.

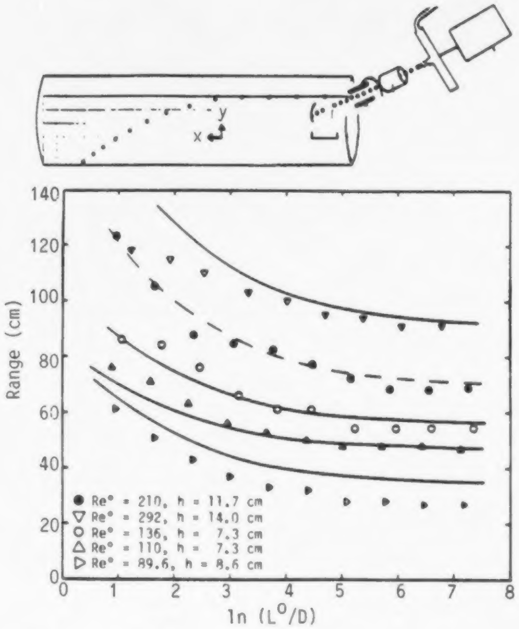


Figure 3. Cold flow trajectory endpoints. The range represents the horizontal distance travelled by the droplet stream while falling a height h. Points represent measured trajectory endpoints; lines represent model results. The solid points and dotted line are data and model results from the best-fit nonlinear regression.

The nominal droplet test condition was: 225 μm initial diameter, 6.5 m/s initial velocity, 130 diameters initial spacing, and 30 degree injection angle. The domain of droplet trajectories observed for this nominal test condition is shown in the two planes of observation in Fig. 5. Superimposed on the cross-sectional view along the centerline axis are lines of constant mean axial velocity of the combustion gases. The droplets were observed to follow an approximately common path until they entered the high shear layer of the reacting gas. The burning times were very short, as indicated by the burning droplet "flecks" stretching only a few centimeters. The large shaded area in Fig. 5 denotes the distribution of burning droplets, igniting and burning out at various locations in this area. Thus, no single trajectory describes a droplet stream test condition. The existence of a domain of droplet stream burnout locations, rather than a single burnout point, is further evidence that the gas velocity fluctuates with time (i.e., turbulence).

Measured droplet axial penetration distances (i.e., axial distance droplet travels prior to complete evaporation) are listed in Table 1. Closely spaced droplets penetrated farther than isolated droplets. Little effect of spacing was observed for values greater than 20 diameters. Axial penetration distance roughly doubled with a doubling of initial droplet velocity. Droplet penetration increased as droplet diameter increased, as well. Little change in axial penetration distance was observed for isolated droplet injection at 0, 30, and 45 degrees. Finally, a change in the combustion gas flow field from a Type C to a Type A flame resulted in a slight reduction in droplet penetration.

Model development to include turbulence effects is ongoing.

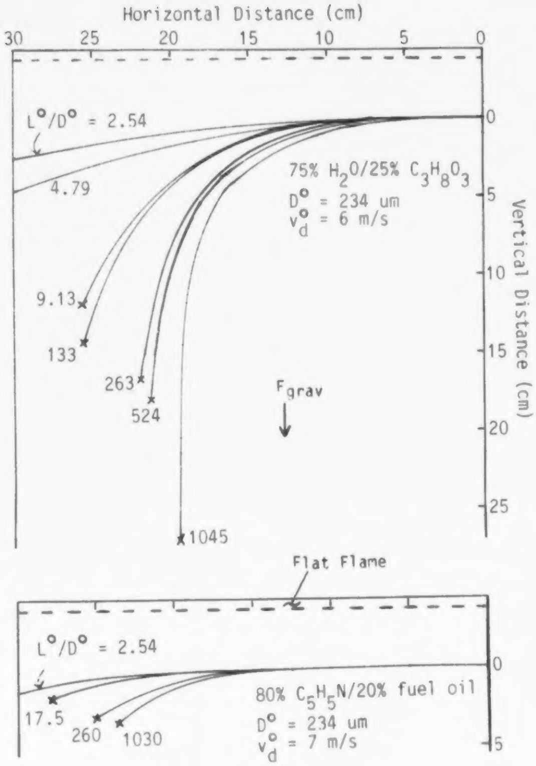


Figure 4. Laminar flow results. The top plot shows trajectories of evaporating, nonburning droplet streams; the bottom plot shows trajectories of burning droplet streams.

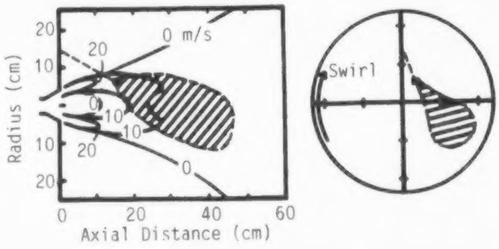


Figure 5. Trajectories of the nominal droplet stream test condition. The shaded area represents the domain of droplet trajectory endpoints. An axial velocity profile is superimposed in the top view.

TABLE 1. MEASURED TRAJECTORIES IN TURBULENT DIFFUSION FLAME EXPERIMENTS

Input Test Condition:		Axial Penetration:		
Variable	Value	Mean	Min.	Max.
Diameter	225 μm	30	15	45 cm
	297	45	35	60
	378	55	45	70
Velocity	3.8 m/s	20	15	25 cm
	6.5	30	15	45
	9.8	45	30	60
Spacing	2.5 dia.	55	35	75 cm
	4.7	45	30	65
	8.8	35	10	55
	16.7	30	10	45
	32.3	30	25	40
	130	30	15	45
Angle	0 deg.	30	20	45 cm
	30	30	15	45
	45	35	25	50
Flame	Type C	30	15	45 cm
	Type A	25	10	35

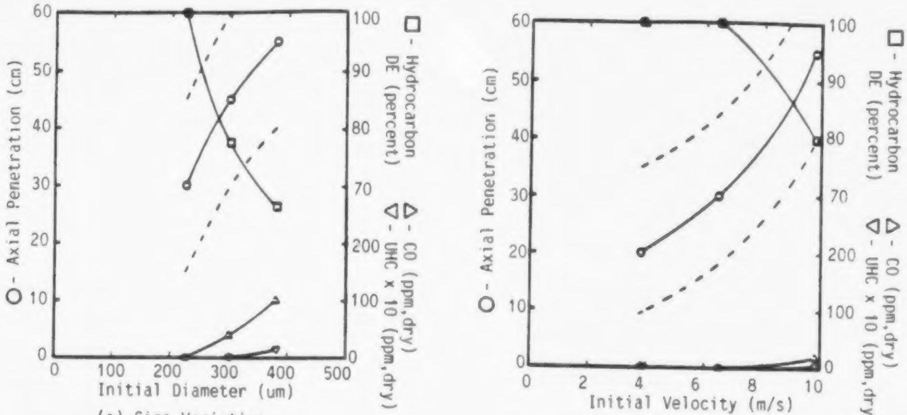
DESTRUCTION EFFICIENCY

Tests were conducted with the water-cooled coil inserted downstream of the Type C flame to quench the combustion gases and measure droplet incineration. Combustion gases were extracted from the stack, with emissions analyzed with and without droplet injection. Droplet destruction efficiency (DE) was calculated as the mass of carbon emitted as CO and UHC divided by the mass of carbon injected.

Droplet incineration results are shown in Fig. 6. The previously measured mean axial penetration is also shown, with dashed lines representing the range of droplet trajectories. These data indicate that droplet destruction efficiency is related inversely to droplet penetration, which has been shown to depend on droplet atomization properties. Thus, predicting droplet ballistics may be one tool for anticipating incinerator failure modes due to poor atomization.

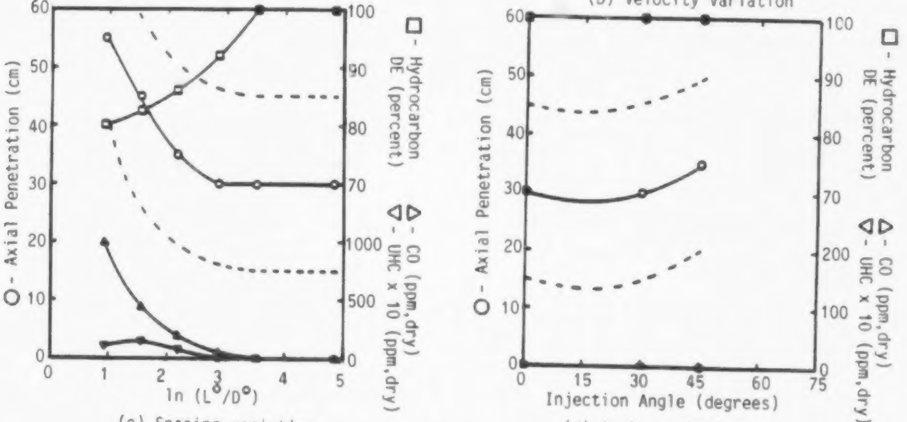
CONCLUSION

Large droplet penetration of the flame zone has been observed as a function of droplet atomization parameters in tests with single monodisperse droplet streams injected into turbulent diffusion flames. The incomplete incineration of these hydrocarbon droplets has been approximated by measuring CO and UHC emissions, and a strong correlation with droplet penetration has been observed. The short burning distances and relatively long trajectories prior to ignition exhibited suggest that droplet aerodynamics prior to ignition is of primary importance in predicting incinerator DRE.



(a) Size Variation

(b) Velocity variation



(c) Spacing variation

(d) Angle variation

Figure 6. Droplet destruction efficiency and axial penetration results.

It was found that in order to predict droplet penetration the model must include:

- Droplet spacing effects on drag.
- Droplet/droplet interaction effects on evaporation rate.
- Evaporation effects on drag.
- Turbulence effects on droplet ballistics.

Cold flow experiments have shown that decreased droplet spacing reduces drag. Laminar flow flat-flame burner experiments have demonstrated that (1) droplet interaction reduces evaporation rate, and (2) mass transfer reduces drag; both effects increase penetration. Turbulent diffusion flame experiments have shown the need for statistically representing droplet penetration. The model is currently being developed to include turbulence effects.

This study represents a first step toward developing a predictive understanding of potential incinerator failure modes due to poor atomization. While it is recognized that further study with full sprays is necessary to establish nozzle operating guidelines based on atomization parameters for incinerators, this ongoing work with monodisperse droplet streams provides a fundamental basis for establishing such criteria.

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DISTRIBUTION OF VOLATILE TRACE ELEMENTS IN EMISSIONS AND RESIDUALS FROM PILOT-SCALE LIQUID INJECTION INCINERATION

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ABSTRACT

The EPA is currently developing regulations on trace element emissions from hazardous waste incineration. However, the data base to support these regulations is very sparse. Data on the effects of waste composition and incinerator operation on trace element emissions are particularly lacking. In response to these data needs, EPA is conducting several test series at the Combustion Research Facility (CRF) Jefferson, AR. The first series of tests was performed to investigate the fate of volatile elements in liquid injection incineration. In these tests, trace amounts of arsenic in the form of arsenic trioxide (As_2O_3) and antimony in the form of antimony trichloride ($SbCl_3$) were fired in a methanol base containing varying amounts of chlorobenzene and carbon tetrachloride. Test variables included incinerator temperature, excess air level, and feed chlorine content. As usually occurs in tests of this type, the data show a general inability to obtain mass balance closure for the trace elements. Both elements are found in the vapor phase at high temperatures, but they condense to particulate at scrubber exit temperatures. Other conclusions await further data reduction and evaluation.

INTRODUCTION

In support of the EPA Office of Solid Waste (OSW) regulation development, the CRF conducted a series of incineration tests to determine the fate of two Appendix VIII metals, antimony and arsenic. These metal-emission tests are important because risk assessments show that metal emissions from otherwise properly operated incinerators can be the largest component of risk to human health and the environment. For these tests, the CRF liquid incinerator system (LIS) fired mixtures of methanol, chlorobenzene, and carbon tetrachloride, spiked with $SbCl_3$ and As_2O_3. The objectives of the test program were:

- To determine the amount and form of arsenic and antimony at various points in the incinerator system
- To provide air pollution control device collection efficiency information
- To measure the distribution of trace elements between flue gas and scrubber blowdown water
- To quantify the relationship between trace element emissions and incinerator operating conditions
- To evaluate whether the presence of trace elements affects other waste emission characteristics

APPROACH

The LIS at CRF incinerates "clean," pumpable and atomizable liquid wastes. Figure 1 shows a simplified schematic of the incinerator system. Combustion takes place in two refractory-lined chambers. The system cleans the combustion product gases in a packed-column scrubber, an ionizing wet scrubber, an activated carbon bed adsorber, and a high-efficiency particulate (HEPA) filter. An induced-draft (ID) fan downstream of the HEPA filter draws a slight vacuum throughout the incinerator/scrubber system and vents the combustion products via a stack.

The test series included variations of three operating parameters: feed chlorine content, incinerator temperature, and combustion excess air. A Box-Wilson factorial experimental design specified 18 test conditions, which included five levels of each parameter. Table 1 lists the planned and achieved conditions. Arsenic and antimony concentrations in the feed were held constant at 12 and 40 ppm, respectively, for all tests. These concentrations in the feed material ensure that the worst-case concentrations in the stack gas will never exceed the threshold limit values (TLVs) of 0.2 mg As/m^3 and 0.5 mg Sb/m^3. Furthermore, if all the trace metals leave the incinerator via the scrubber blowdown water, their concentrations would not exceed the EP toxicity limits (5 mg As/L, no limit established for Sb).

Blends of methanol, carbon tetrachloride, and chlorobenzene in the feed produced the various inlet chlorine concentrations (0 to 28 percent). The liquid feed entered the main combustion chamber via a steam-atomized nozzle at about 45 kg/hr (100 lb/hr). Auxiliary propane maintained the incinerator at the specified temperature that ranged from 1,035° to 1,450°C (1,900° to 2,640°F). Combustion air entered via swirl registers in the burner to produce from 6- to 11-percent excess oxygen at the incinerator exit.

Figure 2 identifies the sampling points and protocols. Continuous monitors, (CMs) measured O_2, CO, and CO_2; volatile organic sampling trains (VOSTs) collected samples at the afterburner and the scrubber exits. Thermal desorption purge and trap GC/ECD was used to evaluate 21 volatile organic compounds.

EPA reference Method 5 was used to collect samples for particulate load and arsenic and antimony analyses. The Method 5 train was modified to ensure collection of antimony and arsenic that passed through the particulate filter. It consisted of a probe and a glass cyclone, followed by a filter and five impingers. The first impinger contained 0.1 N NaOH. The second, third, and fourth impingers contained 0.2 M $(NH_4)_2S_2O_8$ + 0.02 M $AgNO_3$. The last impinger contained silica gel. Following collection and SW-846 digestion, furnace atomic adsorption (AA) methods were used to analyze for arsenic and antimony.

RESULTS

Table 1 shows that 12 out of 18 planned tests were completed. The remaining six test conditions were generally unattainable due to flame stability problems at low flame temperatures. Of the 12 tests for which stable conditions were achieved, data from 7 are currently available. These results are discussed below. A final test report will be published to present all results and conclusions.

Trace Element Discharges

Mass balance for antimony and arsenic could not be established for any of these tests. Table 2 lists the fractions of inlet antimony found at the afterburner exit, the scrubber exit, and the scrubber blowdown water. For each of the tests where the feed had 28-percent chlorine and one of the 18-percent chlorine tests, the samples drawn at the afterburner exit could account for no more than 2 percent of the inlet antimony. Three tests with 18-percent chlorine showed 53 to 146 percent of inlet antimony in the afterburner exit gas. These three are in the range of acceptable mass balance closure based on past experience.

At the scrubber exit, between 7 and 36 percent of the inlet antimony can be accounted for. The higher recovery levels occurred during lower-excess-oxygen tests. Higher combustor temperature also appeared to coincide with with higher recovery at the scrubber exit.

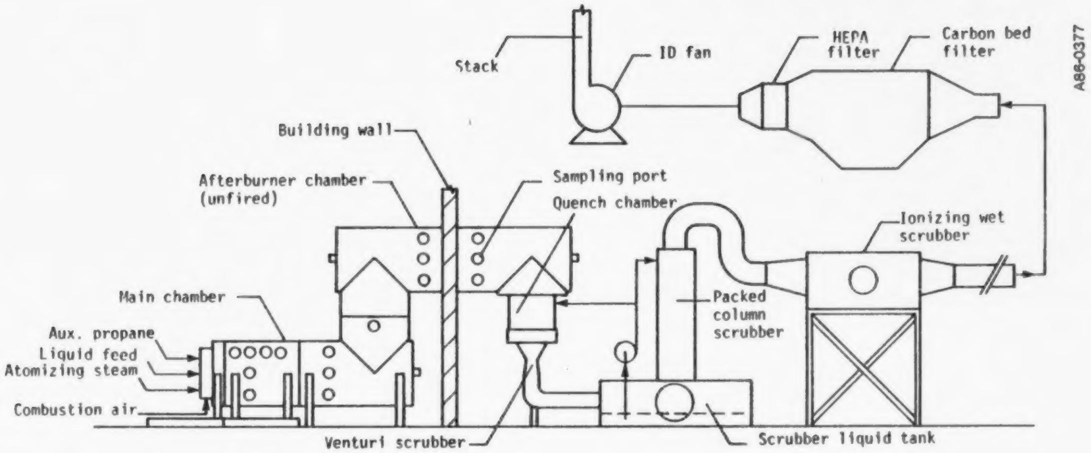
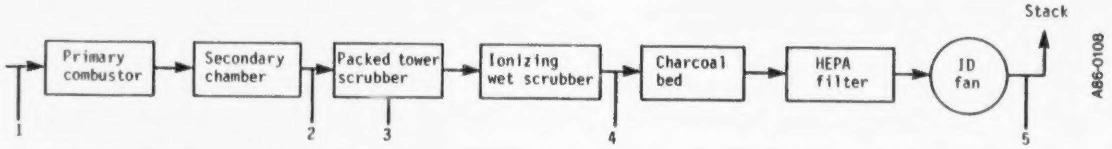

Stack
ID fan
HEPA filter
Carbon bed filter
A88-0377
Building wall
Afterburner chamber (unfired)
Sampling port
Quench chamber
Ionizing wet scrubber
Main chamber
Packed column scrubber
Aux. propane
Liquid feed
Atomizing steam
Combustion air
Venturi scrubber
Scrubber liquid tank

Figure 1. Liquid injection incinerator system.

TABLE 1. SUMMARY OF TEST CONDITIONS

Test no.	Feed Cl content (percent)		Primary combustor temperature (°C (°F))		Afterburner exit O_2 (percent)		Note
	Target	Actual	Target	Actual	Target	Actual	
1	18	--	1,250 (2,280)	-- --	8.4	--	a
2	18	18	1,250 (2,280)	1,336 (2,437)	8.4	8.8	
3	18	18	1,250 (2,280)	1,228 (2,243)	8.4	8.4	b
4	28	28	1,365 (2,490)	1,307 (2,384)	10.1	10.6	
5	28	28	1,130 (2,070)	1,137 (2,079)	10.1	11.0	
6	8	8	1,365 (2,490)	1,290 (2,354)	10.1	10.1	b
7	28	28	1,365 (2,490)	1,399 (2,551)	6.7	6.7	
8	8	--	1,130 (2,070)	-- --	10.1	--	a
9	8	8	1,365 (2,490)	1,425 (2,597)	6.7	5.9	b
10	28	--	1,130 (2,070)	-- --	6.7	--	a
11	8	--	1,130 (2,070)	-- --	6.7	--	a
12	18	--	1,250 (2,280)	-- --	5.5	--	a
13	18	18	1,250 (2,280)	1,203 (2,198)	11.3	11.7	
14	36	35	1,250 (2,280)	1,293 (2,359)	8.4	9.2	b
15	0	0	1,250 (2,280)	1,265 (2,310)	8.4	8.1	b
16	18	18	1,450 (2,640)	1,450 (2,642)	8.4	7.5	
17	18	--	1,045 (1,915)	-- --	8.4	--	a
18	18	17	1,250 (2,280)	1,176 (2,148)	11.3	10.8	

[a] Unable to attain target condition due to unstable flame.
[b] Sample analyses not complete.



	Parameter								
Sampling point	Waste feedrate	Waste feed	Auxiliary fuel feedrate	Air feedrate	Scrubber blowdown	CMs (O_2, CO, CO_2, NO_x)	Volume flow	M5 (particulate, metals)	VOST (volatile organics)
1	X	X	X	X					
2						X	X	X	X
3					X		X		
4							X	X	X
5						X	X	X[a]	

[a] Particulate only.

Figure 2. Sampling protocol.

TABLE 2. ANTIMONY DISCHARGE DISTRIBUTIONS

				Antimony discharge distribution (percent of feedrate)		
Test no.	Feed Cl content (percent)	Primary combustor temperature (°C (°F))	Afterburner exit O_2 (percent)	Afterburner exit flue gas	Scrubber exit flue gas	Scrubber blowdown water
4	28	1,307 (2,384)	10.5	0.18	14	22
5	28	1,137 (2,079)	10.8	0.24	13	16
7	28	1,399 (2,551)	6.1	1.8	30	12
13	18	1,203 (2,198)	11.8	0.11	6.6	87
18	17	1,176 (2,148)	10.7	53.	14	124
16	18	1,450 (2,642)	7.4	146.	36	8.3
2	18	1,336 (2,437)	9.2	104.	20	12

Scrubber blowdown water contained between 8 and 124 percent of the inlet antimony. No clear trend is apparent for these blowdown recovery rates.

Table 3 shows that, at the afterburner exit, where temperatures were above 760°C (1,400°F), the vapor portions of the extracted samples contained an average of 55 percent (range 24 to 90) of the collected antimony. At the scrubber exit where the temperature was 74°C (165°F), the vapor accounted for an average of 8 percent (range 0 to 38) of the collected antimony.

Tables 4 and 5 list the arsenic mass balance and phase distribution data. Except for one test, arsenic recovery was poor. Analyses of collected afterburner exit gas, scrubber exit gas, and blowdown

TABLE 3. ANTIMONY FLUE GAS DISTRIBUTIONS

Test no.	Feed Cl content (percent)	Primary combustor temperature (°C (°F))	Afterburner exit O_2 (percent)	Antimony distribution between particulate and vapor phase in the flue gas (percent)			
				Afterburner exit		Scrubber exit	
				Particulate	Vapor	Particulate	Vapor
4	28	1,307 (2,384)	10.5	62	38	99	1
5	28	1,137 (2,079)	10.8	49	51	62	38
7	28	1,399 (2,551)	6.1	53	47	99	1
13	18	1,203 (2,198)	11.8	42	58	99	1
18	17	1,176 (2,148)	10.7	21	79	100	0
16	18	1,450 (2,642)	7.4	76	24	99.9	0.1
2	18	1,336 (2,437)	9.2	10	90	82	18

TABLE 4. ARSENIC DISCHARGE DISTRIBUTIONS

Test no.	Feed Cl content (percent)	Primary combustor temperature (°C (°F))	Afterburner exit O_2 (percent)	Arsenic discharge distribution (percent of feedrate)		
				Afterburner exit flue gas	Scrubber exit flue gas	Scrubber blowdown
4	28	1,307 (2,384)	10.5	ND	9.0	3.8
5	28	1,137 (2,079)	10.8	ND	5.1	2.3
7	28	1,399 (2,551)	6.1	1.7	58	6.4
13	18	1,203 (2,198)	11.8	ND	ND	2.8
18	17	1,176 (2,148)	10.7	4.0	2.2	3.1
16	18	1,450 (2,642)	7.4	77	9.4	1.9
2	18	1,336 (2,437)	9.2	10.2	4.3	0.51

ND -- Not detected.

Table 5. ARSENIC FLUE GAS DISTRIBUTIONS

Test no.	Feed Cl content (percent)	Primary combustor temperature (°C (F°))	Afterburner exit O_2 (percent)	Arsenic distribution between particulate and vapor phase in the flue gas (percent): Afterburner exit — Particulate	Afterburner exit — Vapor	Scrubber exit — Particulate	Scrubber exit — Vapor
4	28	1,307 (2,384)	10.5	ND	ND	100	0
5	28	1,137 (2,079)	10.8	ND	ND	83	17
7	28	1,399 (2,551)	6.1	43	57	100	0
13	18	1,203 (2,198)	11.8	ND	ND	ND	ND
18	17	1,176 (2,148)	10.7	32	68	100	0
16	18	1,450 (2,642)	7.4	76	24	100	0
2	18	1,336 (2,437)	9.2	83	17	94	6

ND -- Not detected.

water samples could account for no more than 10 to 15 percent of the incoming arsenic. The general low recovery rates rendered it difficult to identify any trends. However, it was apparent that most, if not all, of the collected arsenic was found on the particulate portion of the sample train. This is in agreement with the antimony results.

Destruction and Removal Efficiencies (DREs)

The tests demonstrated high DREs for both carbon tetrachloride and chlorobenzene (Table 6). Chlorobenzene DREs were higher than those for carbon tetrachloride. Carbon tetrachloride DREs were greater than 99.99 percent at the afterburner exit. These increased to greater than 99.999 percent at the scrubber exit. Similarly, chlorobenzene DREs ranged from 99.999 percent at the afterburner exit to greater than 99.9999 percent at the scrubber exit. The available data do not suggest any discernible effect of temperature, feed composition nor excess air. This is in general agreement with previous CRF data, which has consistently shown high DREs for concentrated feed materials.

Products of Incomplete Combustion (PICs)

Incineration produces low levels of PICs. The CRF routinely analyzes VOST samples for 21 organic compounds with GC/ECD. Tables 7 and 8 summarize the higher concentration compounds found during these tests. At the afterburner exit, carbon tetrachloride (POHC) was highest among the 21 compounds (>100 μg/dscm). Other chlorinated alkanes and alkenes were present in the 10- to 100-μg/dscm range. Chlorobenzene (POHC) concentrations were similar to those of the common chlorinated PICs.

At the scrubber exit, PIC concentrations are about one-tenth of those at the scrubber inlet; i.e., afterburner exit. Carbon tetrachloride (a POHC) ranged from 4 to 23 μg/dscm. The highest concentration occurred at a low excess air condition. Chlorobenzene (the other POHC) ranged from 1 to 4 μg/dscm and did not appear to correlate with temperature or excess air. Other PICs include methylene chloride, which is ever-present at high levels (15 to 67 μg/dscm). Chloroform was also present and ranged from 9 to 74 μg/dscm. Other chlorinated alkanes and alkenes, hexane, benzene, and toluene were below 10 μg/dscm.

DISCUSSION

The data evaluated to date point to the lack of mass balance closure for the trace volatile elements. The exact cause for the low recovery rates for the two elements at

TABLE 6. POHC DREs

Test no.	Afterburner exit O_2 (percent)	Combustor Temperature (°C (°F))	Carbon tetrachloride			Chlorobenzene		
				DRE (percent)			DRE (percent)	
			Feed concentration (percent)	Afterburner exit	Scrubber exit	Feed concentration (percent)	Afterburner exit	Scrubber exit
4	10.5	1,307 (2,384)	22	99.9988	--[a]	24	99.9996	--
5	10.8	1,137 (2,079)	24	--	99.999945	22	--	99.999984
13	11.8	1,203 (2,198)	11	--	99.99983	24	--	99.999987
18	10.7	1,176 (2,148)	11	--	99.99973	23	--	99.999981
16	7.4	1,450 (2,642)	11	--	99.99953	24	--	99.999981
2	9.2	1,336 (2,437)	11	99.9982	99.99985	23	99.999995	99.999985

[a] Data not available; sampling train contamination occurred.

TABLE 7. AFTERBURNER EXIT PIC DATA

Test no.	4	2
Afterburner exit O_2 (percent)	10.5	9.2
Primary combustor temperature (°C (°F))	1,307 (2,384)	1,336 (2,437)
POHC concentration (μg/dscm)		
Carbon tetrachloride	110	150
Chlorobenzene	37	11
PIC concentration (μg/dscm)		
Methylene chloride	18	77
1,1-dichloroethylene	38	6.7
Chloroform	70	12
1,2-dichloroethylene	38	58
Trichloroethylene	21	14
Benzene	13	3
1,1,2-trichloroethane	61	23
Hexane	15	10
Toluene	12	11

TABLE 8. SCRUBBER EXIT PIC DATA

Test no.	5	13	18	16	2
Afterburner exit O_2 (percent)	10.8	11.8	10.7	7.4	9.2
Primary combustor temperature (°C (°F))	1,137 (2,079)	1,203 (2,198)	1,176 (2,148)	1,450 (2,642)	1,336 (2,437)
POHC concentration (μg/dscm)					
Carbon tetrachloride	4.4	7.5	12	23	12
Chlorobenzene	1.6	1.4	1.6	1.8	4.0
PIC concentration (μg/dscm)					
Methylene chloride	15	34	42	67	18
1,1-dichloroethylene	0.6	ND	ND	ND	ND
Chloroform	74	8.9	8.8	18	25
1,2-dichloroethylene	8.7	ND[a]	ND	2.4	3.1
1,1,1-trichloroethane	0.2	0.8	0.6	1.0	1.3
Trichloroethylene	1.3	1.9	3.3	2.1	1.6
Benzene	2.6	1.3	1.6	1.0	6.3
1,1,2-trichloroethane	9.5	1.9	0.5	5.2	ND
Hexane	0.9	1.9	5.5	2.0	2.0
Toluene	1.6	1.9	8.0	2.7	4.0

ND -- Not detected.

the afterburner are not known. It may be due to inconsistent capture efficiencies or the sampling train's ability to capture these volatile metals. Other unknown factors may play a role in the sampling train's performance.

The information obtained to date tends to suggest the following:

- The presence of trace amounts of antimony and arsenic does not affect POHC DRE.
- Both arsenic and antimony appear to show up in considerably greater amounts as solids, especially at lower temperatures.

The data reported here are complex. Trends identified earlier are weak at best. Upon completion of the sample analysis of the remaining test samples, a clearer picture may emerge. These will be reported in the test final report, to be submitted at the conclusion of the test program.

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ASSESSMENT OF RESIDUES FROM INCINERATION OF RCRA WASTES

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ABSTRACT

Incineration is generally recognized as a well-demonstrated technology for the treatment of organic hazardous wastes including spent solvent wastes. Most studies of incineration have been concerned with the effectiveness of the process to destroy key organic constituents of a waste (destruction and removal efficiency, DRE) as measured by the relative quantity of those organics in the incinerator off-gas. In contrast, this paper focuses on characterization of the solid and liquid residues generated by incineration of RCRA wastes.

Two incineration systems are evaluated - one at a commercial treatment, storage and disposal facility (TSDF) accepting organic wastes from a variety of industrial generators (Facility A) and the other operated on-site at a chemical industry manufacturing plant (Facility B). Both systems generate two types of residue - ash and scrubber wastewater. Ash from both facilities is currently landfilled. Treatment of the scrubber wastewater at Facility A results in a metal sulfide sludge, which is also landfilled. At Facility B, scrubber wastewater is neutralized and injected into a deepwell on site.

All ash, sludge and wastewater samples collected at these facilities were analyzed for priority pollutant organics and metals. The ash and sludge samples were also subjected to the Toxicity Characteristic Leaching Procedure (TCLP). Ash from Facility A exhibited unacceptably high TCLP extract concentrations of two volatile organics - methylene chloride and tetrachloroethylene, indicating incomplete combustion of solvent wastes. Ash from facility B passed the TCLP for both metals and organics, but both ash and extract levels of three non-TCLP metals - Copper, Nickel, and Zinc - were high. Scrubber wastewater from both facilities had no significant concentrations of toxic organics. However, copper, lead, nickel and zinc were found at concentration greater than 50 mg/l in the scrubber wastewater from Facility B. This paper presents and evaluates quantitative data describing the wastes incinerated and the resulting residues at both facilities.

INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 call for a ban on the land disposal of hazardous wastes. EPA is required to evaluate technologies for each waste category and to establish treatment performance levels for wastes based on the lowest levels achieved by a "best demonstrated available technology". Treatment levels from incineration have been selected for F001-F005 spent solvents. Incineration is also likely to be an important technology for most other listed organic wastes. Therefore, the quantity, chemical characteristics, and fate of incineration residuals are important.

Incineration is a controlled high temperature oxidation process by which organic wastes are destroyed. The combustion reactions of incineration should convert organic wastes to gaseous CO_2 and water vapor. If the waste contains chlorinated organics, then HCl and free chlorine gas are also generated as incineration byproducts. Incineration of wastes containing organic sulfur or nitrogen results in formation of SOx and NOx, respectively. Air pollution control devices - often wet scrubbers - are used to control emissions from hazardous waste incinerators.

The residues from incineration are the off-gas, ash and scrubber wastewater.

The effectiveness of an incinerator and its associated air pollution system is normally measured in terms of destruction and removal efficiency (DRE), as defined by the following formula:

$$DRE = \frac{Win-Wout}{Win} \times 100\%$$

Win = mass feed rate of the principal hazardous constituent(s) to the incinerator

Wout = mass emission rate of the principal organic hazardous constituent(s) to the atmosphere as measured in the stack prior to discharge.

This formula considers only off-gas emissions to the atmosphere, ignoring the other residuals of incineration - ash and scrubber wastewater.

Samples of wastes, ash and scrubber wastewater were collected from two full-scale incineration facilities as part of a program to evaluate alternatives to land disposal. This paper summarizes the operations at both facilities and presents and evaluates quantitative data describing the wastes incinerated and the resulting residues.

FACILITY A

Facility Description

Facility A is a commercial hazardous waste treatment facility accepting drummed organic hazardous wastes from a variety of industrial generators. Typical wastes accepted for incineration at Facility A include chlorinated and nonchlorinated solvent wastes (F001, F002, F003, F004, F005), paint formulating wastes, furniture strippers, printing inks and dyes, polymer wastes, agricultural products, pharmaceutical production wastes, lab packs and contaminated soils. The facility does not accept PCBs, dioxins, compressed gases, radioactive waste, or organic wastes containing significant concentrations of potassium, sodium, lithium, mercury or lead.

Figure 1 shows a process flow diagram for Facility A. Waste organic liquids are pumped from drums into one of four 6000 gallon steel blend tanks. Waste liquids are selected such that the final blend has greater than 8000 BTU/lb and less than 40% chlorine.

Drums containing primarily solids, nonpumpable materials or residues remaining from liquid pumping are transported to the drum processing building. Operators use an air-driven cutting tool to remove the tops of steel drums. Drums are then upended and dumped

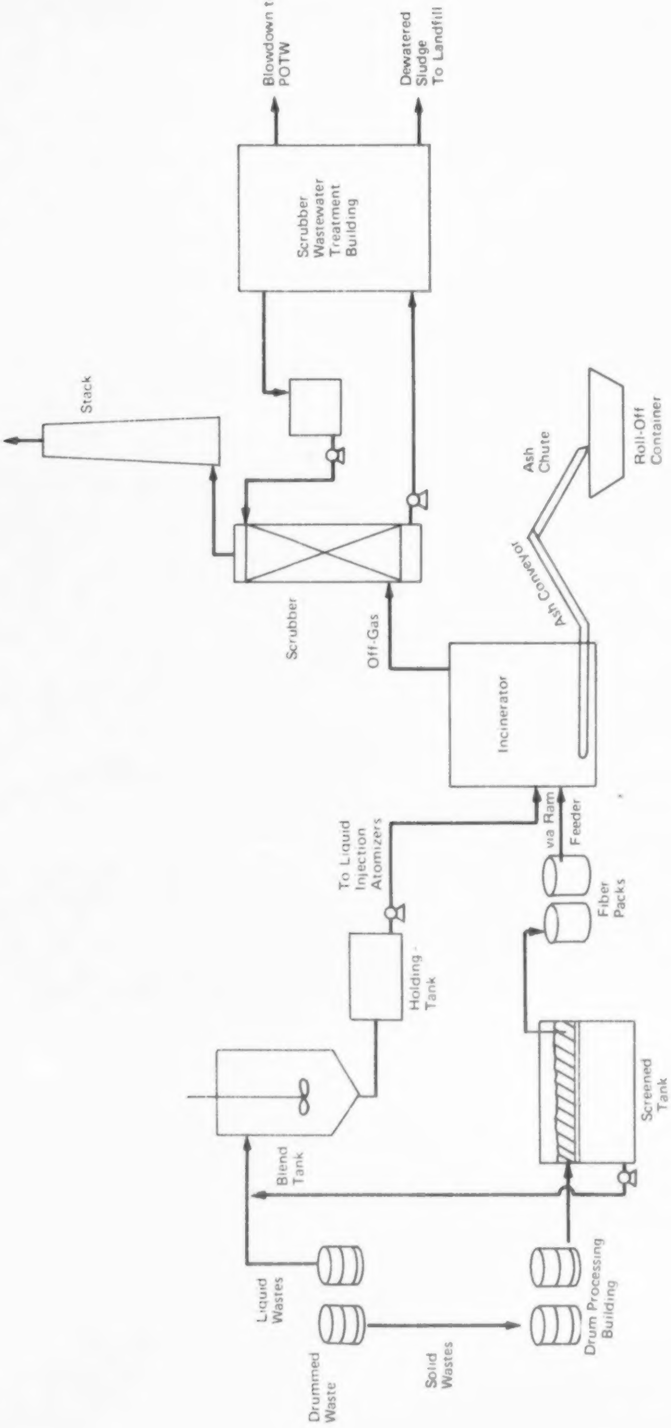
Drummed Waste
Liquid Wastes
Solid Wastes
Drum Processing Building
Blend Tank
Screened Tank
Holding Tank
To Liquid Injection Atomizers
Fiber Packs
via Ram Feeder
Incinerator
Ash Conveyor
Ash Chute
Roll-Off Container
Off-Gas
Scrubber
Stack
Scrubber Wastewater Treatment Building
Blowdown to POTW
Dewatered Sludge To Landfill

Figure 1. Facility A process flow diagram.

onto a coarse-mesh screen above a steel tank. Any free liquids drain into the tank and are subsequently pumped to a blend tank. Solids remaining on the screen are shoveled into 30 gallon fiber packs. Empty drums are steam-cleaned, and the cleaning solutions are added to a blend tank.

The incinerator at Facility A is a dual chamber unit with a thermal input rating of 19.8 million BTU/hr. All wastes are introduced into the lower chamber. Liquid waste from the blend tank is injected into this chamber by atomization with steam. Solids in fiber packs are loaded into the incinerator by a ram feeder. Solids residence time in the lower chamber is estimated at 15 to 30 minutes. The upper chamber is an afterburner used to complete combustion. Fuel oil is burned in this chamber to maintain required temperature.

Dry ash residue is conveyed from the lower chamber out of the incinerator building and is dumped into a roll-off container. The ash is transported off-site to a permitted hazardous waste landfill.

A caustic scrubber is employed for removing air pollutants, particularly HCl, from the stack gas. This scrubber permits burning wastes with up to 40 percent total chlorine content.

The approximate feed and effluent flowrates during the sampling period were as follows:

Feed
Solid waste = 48.1 ft^3/hr
Liquid waste = 28.3 ft^3/hr

Residuals
Bottom Ash = 5.25 ft^3/hr
Scrubber Wastewater = 722 ft^3/hr

Scrubber wastewater treatment includes pH adjustment, hydroxide and sulfide precipitation of heavy metals, clarification, pressure chamber filtration, and sludge dewatering with a recessed plate filter press (Figure 2).

Scrubber water collects in a 400 gallon steel tank and is pumped to the scrubber wastewater treatment building. The wastewater flow is typically 90 gpm.

The wastewater pH is adjusted to 9.0 with 25 percent caustic in a 7,000-gallon mixed tank. Sodium sulfide is added to precipitate heavy metal sulfides which remain in solution after hydroxide precipitation at pH 9.0. Ferric chloride is added to this tank as a conditioning agent to improve clarification and filtration. High cationic synthetic polyelectrolyte polymer is added before an in-line static mixer as the wastewater is pumped to the clarifier.

Wastewater is clarified in a 20,000 gallon steel tank which overflows to a second 20,000 gallon steel storage tank. Clarified effluent is then pumped through a seven element filter. The elements are operated in a parallel and each element contains a 200 mesh polypropylene filter bag. The filter is backwashed once each shift, and the backwash water is returned to the clarifier.

A portion of the treated, filtered wastewater is recycled to the scrubber. A blowdown stream is stored in a third 20,000 gallon steel tank. Blowdown wastewater from this storage tank is trucked periodically to the municipal wastewater treatment plant.

Sludge from the clarifier is pumped to a 7000 gallon steel conditioning tank. Synthetic polyelectrolyte is added to this mixed tank as a filter aid. The conditioned sludge is pumped to a recessed plate filter press once each shift. The filtrate is returned to the clarifier, and the dewatered sludge is collected for landfill disposal.

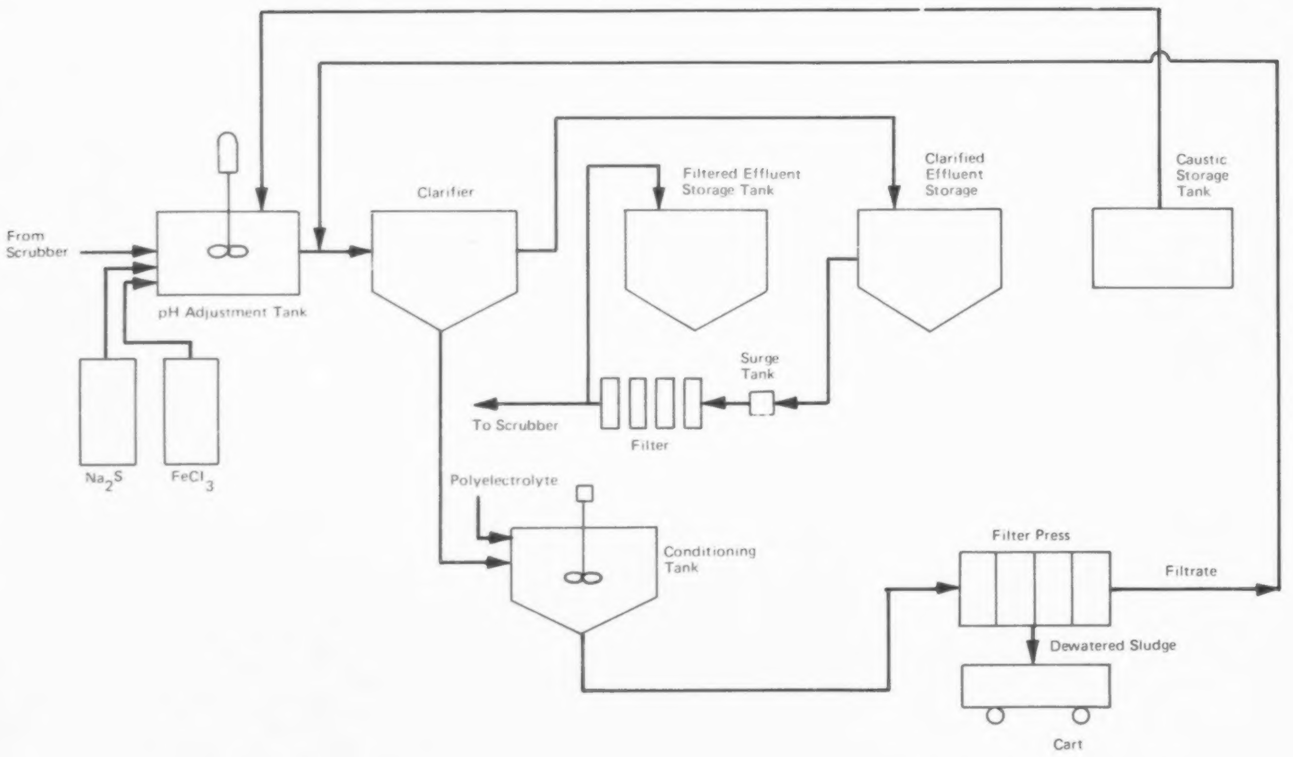
From Scrubber
pH Adjustment Tank
Na_2S
$FeCl_3$
Clarifier
Filtered Effluent Storage Tank
Clarified Effluent Storage
Caustic Storage Tank
Surge Tank
To Scrubber
Filter
Polyelectrolyte
Conditioning Tank
Filter Press
Filtrate
Dewatered Sludge
Cart

Figure 2. Facility A scrubber wastewater treatment.

Waste Characterization

During a week-long sampling program, samples of five discrete solid wastes and five discrete liquid wastes were obtained. In addition, a sample of the liquid waste from the blend tank was taken. As Table 1 shows, the major volatile organic components of these wastes were the common solvent compounds acetone, benzene, chloroform, methylene chloride, methyl ethyl ketone, tetrachloroethylene, toluene, trichloroethylene and xylene. These nine components account for about 54 percent by weight of the liquid waste blend. Surprisingly, the liquid waste contained 28.7 weight percent water and its fuel value was only 6,824 BTU/lb, below the plant's stated goal of ≥8000 BTU/lb. The liquid blend's organic chloride content of 27.99 percent was below the plant's stated upper limit of 40 percent.

The five solid wastes represent diverse industrial sources. Information supplied to Facility A by the waste generators indicates that the five solid wastes were (1) epoxy resins, (2) used nylon mesh filter bags, (3) waste tetrachloroethylene and wax mixture, (4) waste methylene chloride and polymer, and (5) eye shadow with tetrachloroethylene.

Measureable levels of chromium, copper, lead, nickel and zinc were found in all waste samples. The highest metal concentration was 759 mg/L copper in the liquid waste blend.

Residue Characterization

The wastes described in the previous section were incinerated during a 36-hour period. Beginning 4 hours after the first fiberpack of solid waste was fed to the incinerator, grab samples of ash were collected from the ash chute every two hours until the incineration run was complete. The individual grab samples were composited to form a single ash residue sample representative of the burn. Tables 2 and 3 summarize the analytical data for this sample.

Compositional analysis of the ash shows significant concentrations of several volatile and semivolatile organic compounds. The toxicity characteristic leaching procedure was run on the ash sample. Extract levels of two volatile organics - methylene chloride and tetrachloroethylene - exceed the regulatory levels for these compounds, meaning that the ash must be classified as a hazardous waste.

Metals appear to have concentrated in the ash as expected, with most metals present in the ash at levels greater than their concentrations in any of the waste samples. Arsenic exhibits the greatest concentration factor. Its ash concentration - 42 mg/kg - is 52 times the highest waste sample arsenic concentration. Copper at 13,800 mg/kg is the major metal component of the ash. Both TCLP and EP extracts were analyzed for toxic metals. None of the eight listed EP Toxicity metals were found above regulatory levels in either extract. Comparison of extract and compositional metals levels indicates that the ash is fairly resistant to leaching of metals.

The ash had a total solids content of about 60 percent by weight and a specific gravity of 1.28.

Data on the scrubber wastewater and its treatment products are summarized in Table 4. With the exception of acetone which was also found in the laboratory blank, none of the organic compounds measured in the wastes or ash were detected in the scrubber wastewater or the filtered effluent.

Seven toxic metals were reported above detection levels in the scrubber wastewater at concentrations ranging from 0.6 mg/L for arsenic to 11.0 mg/L for copper. Metal concentrations in the

Table 1. Facility A Waste Characterization

PARAMETER	Liquid Blend	Solid #1 Epoxy Resins	Solid #2 Solvent Filter Bags	Solid #3 Waste Tetrachloroethylene and Wax	Solid #4 Waste Methylene Chloride & Polymer	Solid #5 Eye Shadow with Tetrachloroethylene
VOLATILE ORGANICS (ppb)						
Acetone	4,035,100	210,000	<23,000	<24,000	<24,000	<25,000
Benzene	20,000	<5,000	<12,000	<12,000	<12,000	<12,000
Chloroform	29,300	<5,000	<12,000	<12,000	<12,000	<12,000
Methylene Chloride	46,413,200	<5,000	<12,000	<12,000	34,000,000	<12,000
Methyl Ethyl Ketone	2,937,900	<10,000	<23,000	<24,000	<24,000	<25,000
Tetrachloroethylene	385,904,000	<5,000	<12,000	260,000,000	580,000	220,000,000
Toluene	140,366,500	32,350,000	8,900,000	100,000	<56,000	24,000
Trichloroethylene	1,372,600	<5,000	<12,000	8,600,000	<12,000	<12,000
Xylene	828,000	9,242,500	<12,000	<12,000	620,000	<12,000
TOXIC METALS (ppm)						
Antimony	<1.0	<1.0	<1.0	<1.0	<1.0	4.0
Arsenic	0.19	<0.1	0.8	0.1	<0.1	0.1
Barium	111	41.0	70.0	<1.0	<1.0	125
Beryllium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cadmium	<0.5	<0.5	1.3	<0.5	0.7	1.2
Chromium-hexavalent	1.83	<0.01	0.540	0.097	0.350	0.300
Chromium-total	20.3	12.0	61.0	12.0	0.8	40.0
Copper	759	13.0	43.0	11.0	2.0	75.0
Lead	34.6	20.0	110.0	2.0	6.0	5.0
Mercury	0.16	<0.1	1.4	<0.1	0.2	0.3
Nickel	8.7	12.0	70.0	45.0	0.8	6.0

Table 1. (Continued) Facility A. Waste Characterization

PARAMETER	Liquid Blend	Solid #1 Epoxy Resins	Solid #2 Solvent Filter Bags	Solid #3 Waste Tetrachloroethylene and Wax	Solid #4 Waste Methylene Chloride & Polymer	Solid #5 Eye Shadow with Tetrachloroethylene
Selenium	1.6	7.0	7.0	6.0	3.0	<1.0
Silver	<0.2	<0.2	0.4	<0.2	<0.2	<0.2
Thallium	<1.0	<1.0	3.0	3.0	<1.0	2.0
Zinc	61.2	8.0	105.0	19.0	7.0	1100.0
OTHER ANALYSES						
WT % Carbon	32.25	68.60	4.89	80.95	13.70	9.64
WT % Hydrogen	7.02	9.08	3.40	9.51	9.44	7.07
WT % Water	28.7	0.49	32.88	1.15	11.25	1.38
WT % Organic Halide	27.99	0.31	0.57	52.41	24.47	22.91
Sp. Gravity	1.084	1.0215	1.3745	1.3135	1.1105	1.5954
Total Solids (mg/kg)	156,000	745,100	581,200	250,800	428,600	662,800
BTU/lb.	6,824	15,850	DNI	5,750	7,019	4,021

DNI = Does Not Ignite

Table 2. Facility A Ash Analytical Data* - Organics

PARAMETER	Compositional (μg/kg)	TCLP Extract (μg/L)	Regulatory Level (μg/L)
Volatile Organics			
Methylene chloride	38,000	8,800	8,600
Acetone	20,000	<3,300	None
Chloroform	46	<1,700	70
2-Butanone	2,000	<3,300	7,200
1,1,1 trichloroethane	12	<1,700	30,000
1,2 dichloropropane	32	<1,700	None
trichloroethylene	120	<1,700	70
benzene	42	<1,700	70
4-methyl-2-pentanone	2,300	<3,300	None
tetrachloroethylene	1,200,000	48,000	100
toluene	2,500	11,000	14,400
chlorobenzene	27	<1,700	1,400
ethylbenzene	380	<1,700	None
styrene	320	<1,700	None
xylenes	1,900	<1,700	None
methanol	410,000	N.M.	None
Semivolatile Organics			
Phenol	40,000	<1,400	14,400
Nitrobenzene	29,000	<200	130
2,4 dimethyl phenol	23,000	<1,000	None
naphthalene	24,000	310	None
2-nitroaniline	180,000	1,300	None
dimethyl phthalate	55,000	370	None
diethyl phthalate	120,000	410	None
di-n-butyl phthalate	160,000	<200	None

*Analysis of a single composite sample. Aliquots of ash making up the composite were collected every two hours during the incineration run.

Table 3. Facility A Ash Analytical Data* - Metals

PARAMETER	Compositional (mg/kg)	TCLP Extract (mg/L)	EP Toxicity Extract (mg/L)	Regulatory Level (mg/L)
Toxic Metals				
Antimony	8.0	0.094	<1.0	None
Arsenic	42.0	0.062	0.2	5.0
Barium	150	0.026	<1.0	100.0
Beryllium	<0.2	<0.005	<0.2	None
Cadmium	2.0	0.02	<0.5	1.0
Hexavalent Chromium	0.083	NM	NM	None
Total Chromium	71.0	0.01	<0.3	5.0
Copper	13,800	0.729	4.0	None
Lead	30.0	<0.05	<1.0	5.0
Mercury	0.2	0.00025	<0.1	0.2
Nickel	190	1.14	2.0	None
Selenium	<1.0	<0.001	<1.0	1.0
Silver	0.4	<0.005	<0.2	5.0
Thallium	2.0	<0.001	<1.0	None
Zinc	280	1.15	0.3	None
Other Analyses				
Total solids (mg/kg)	599,300	-	-	-
Specific gravity (g/mL)	1.2809	-	-	-
Paint Filter Test	PASS	-	-	-

*Analysis of a single composite sample. Aliquots of ash making up the composite were collected every two hours during the incineration run.

Table 4. Facility A Scrubber Wastewater Treatment Data

PARAMETER	Scrubber Wastewater (pH Tank)	Filtered Effluent	Dewatered Sludge	Dewatered Sludge EP Toxicity Extract
Volatile Organics (µg/l)				
Methylene Chloride	<5.0	<5.0	390 B	-
Acetone	32 B	28 B	170 B	-
Chloroform	<5.0	<5.0	<18	-
Methyl ethyl ketone	<10.0	<10.0	<36	-
1,1,1 trichloroethane	<5.0	<5.0	<18	-
1,2 dichloropropane	<5.0	<5.0	<18	-
trichloroethylene	<5.0	<5.0	<18	-
benzene	<5.0	<5.0	<18	-
4-methyl-2-pentanone	<10.0	<10.0	<36	-
tetrachloroethylene	<5.0	<5.0	<18	-
toluene	<5.0	<5.0	<18	-
chlorobenzene	<5.0	<5.0	<18	-
ethyl benzene	<5.0	<5.0	<18	-
styrene	<5.0	<5.0	<18	-
xylenes	<5.0	<5.0	<18	-
methanol	NM	NM	NM	-
Semivolatile Organics (µg/L)				
Phenol	<20.0	<20.0	<740	-
Nitrobenzene	<20.0	<20.0	<740	-
2,4 dimethyl phenol	<20.0	<20.0	<740	-
naphthalene	<20.0	<20.0	3,600	-
2-nitroaniline	<100	<100	<3,700	-
dimethyl phthalate	<20.0	<20.0	<740	-
diethyl phthalate	<20.0	<20.0	<740	-
di-n-butyl phthalate	<20.0	<20.0	<740	-

Table 4. (Continued) Facility A Scrubber Wastewater Treatment Data

PARAMETER	Scrubber Wastewater (pH Tank)	Filtered Effluent	Dewatered Sludge	Dewatered Sludge EP Toxicity Extract
Toxic Metals (mg/L)				
Antimony	4.0	<1.0	313	<1.0
Arsenic	0.6	0.5	140	0.2
Barium	<1.0	<1.0	183	<1.0
Beryllium	<0.2	<0.2	<0.2	<0.2
Cadmium	0.7	<0.5	400	<0.5
Hexavalent Chromium	0.526	0.063	<0.01	NM
Total Chromium	1.4	<0.3	55	<0.3
Copper	11.0	5.0	8300	1.0
Lead	2.0	1.3	1600	<1.0
Mercury	<0.1	<0.1	60	<0.1
Nickel	4.0	1.7	2200	<0.3
Selenium	<1.0	<1.0	<1.0	<1.0
Silver	<0.2	<0.2	0.6	<0.2
Thallium	<1.0	<1.0	3.0	<1.0
Zinc	8.0	5.0	3100	0.5
Other Analyses				
Total Solids (mg/L)	86,600	65,700	450,400	-
Total Dissolved Solids (mg/L)	82,500	65,400	NM	-
Total Suspended Solids (mg/L)	670	360	NM	-
Specific Gravity	1.0540	1.0373	1.2921	-
pH	>12	>12	NM	-
Alkalinity (mg/L as $CaCO_3$)	NM	NM	37,888	-

NM = not measured

B = Analyte found in blank as well as in sample. Value shown has not been corrected for blank contamination.

filtered effluent are less than those of the scrubber wastewater.

No information is available on Facility A's discharge permit to the local POTW. However, strictly for purposes of comparison, Table 5 presents filtered effluent data for five metals along with the daily maximum concentrations of metals permitted to be discharged to publicly owned treatment works (POTWs) by metal finishing operations (Effluent Guidelines for Metal Finishing. Amended September, 1984). Facility A's effluent exceeds the metal finishing effluent guidelines concentrations for copper, lead and zinc.

The dewatered sludge from scrubber wastewater treatment was about 45 percent total solids by weight. Metals concentrations in the sludge were greater than 1000 ppm for copper, lead, nickel and zinc. An EP Toxicity test was done on this sludge. None of the metals exceeded regulatory levels in the extract.

FACILITY B

Facility Description

Facility B is a chemical manufacturing plant owned and operated by a major chemical company. Both solid and liquid hazardous organic wastes generated at Facility B and at several of the company's other plants are incinerated at Facility B.

Solid wastes and sludges are received in drums and typically include paint sludges, chlorinated hydrocarbons, coke solids, vacuum filter solids, waste filter elements and polymeric tar.

Liquid wastes are transported by tanker truck and are transferred on site to one of four 20,000 gallon waste storage tanks. One is used as a feed tank, another as a waste blending tank, and the remaining two as holding tanks. Liquid wastes commonly include waste organic solutions, waste solvents, tank farm nitriles and chloroprene catalyst sludge.

The incineration system (Figure 3) at Facility B includes both a rotary kiln incinerator and a single-stage liquid injection incinerator. The total system thermal input rating is 40 million BTU/hr. Both the incinerators use natural gas as auxiliary fuel. The liquid injection incinerator burns only liquid wastes, which are predominantly generated from the manufacturing operations on site. Ash is removed about four times per year from the liquid injection incinerator. The rotary kiln incinerator will typically burn the same liquid wastes, in addition to a variety of solid wastes.

Solid wastes are all contained in drums. The drums are fed to the kiln by an automated feed system. First the drum top is removed, and the drum is lifted vertically up an elevator. It is then transported horizontally across a conveyor. The drum then enters an airlock before being inverted and the contents dumped into the rotary kiln. Empty drums are returned down the elevator and placed in storage. If the drums must be cleaned they are washed with toluene or water and set out to dry. The toluene and water wastes are also incinerated.

The rotary kiln is followed by a natural gas-fired afterburner designed to further burn gases exiting the kiln. Normal operating temperatures for the rotary kiln are 1200-1400°C. Afterburner temperatures for the rotary kiln are 100-150°C higher than the kiln. Average solid residence times in the kiln are between 40 and 60 minutes, and the kiln rotation is between 0.10 and 0.20 revolutions per minute. Ash is discharged continuously from the kiln to an ash sluice.

Liquid wastes, as described previously, are stored in four (20,000 gallon) tanks. These tanks are recirculated by pumps to mix the tank contents. It normally takes 2 to 3 days to burn the contents of one tank.

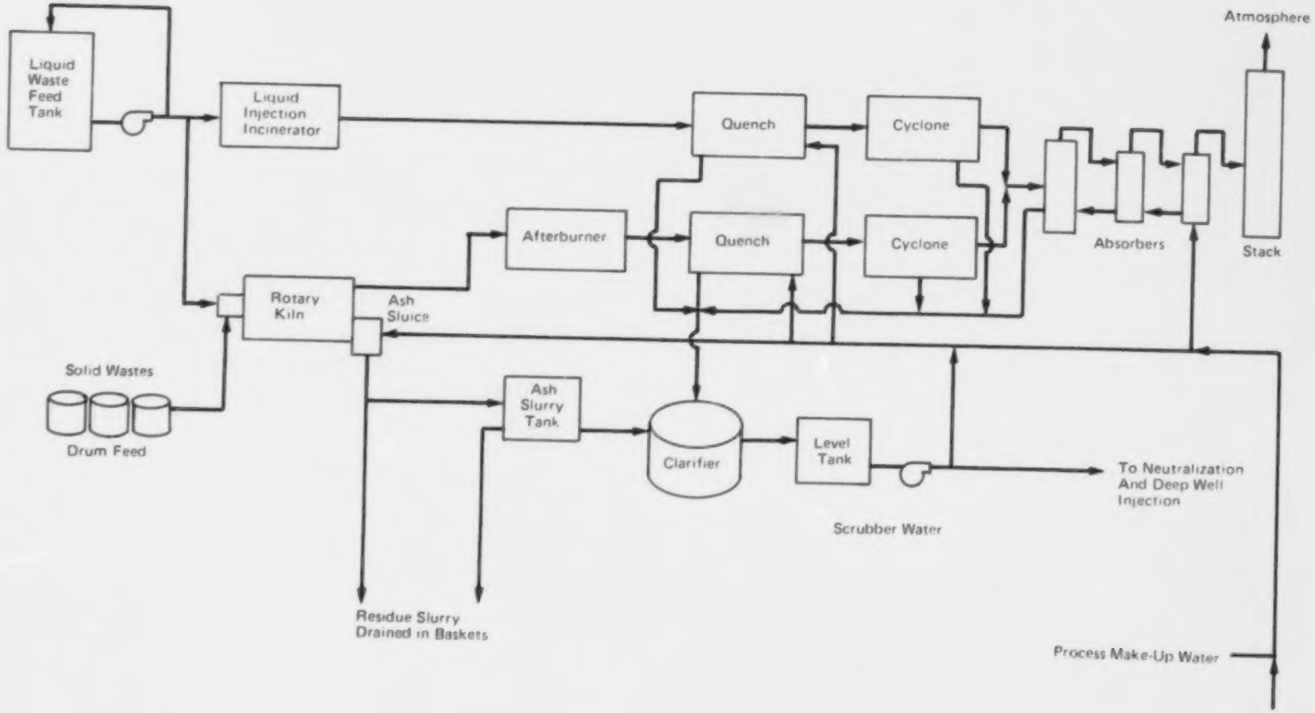
Liquid Waste Feed Tank
Liquid Injection Incinerator
Quench
Cyclone
Atmosphere
Afterburner
Quench
Cyclone
Absorbers
Stack
Rotary Kiln
Ash Sluice
Solid Wastes
Drum Feed
Ash Slurry Tank
Clarifier
Level Tank
To Neutralization And Deep Well Injection
Scrubber Water
Residue Slurry Drained in Baskets
Process Make-Up Water

Figure 3. Facility B process flow diagram.

TABLE 5. FACILITY A EFFLUENT METALS

Metal	Filtered Effluent (mg/L)	Metal Finishing Effluent Guidelines (mg/L)
Copper	5.0	3.38
Nickel	1.7	3.98
Lead	1.3	0.69
Chromium	<0.3	2.77
Zinc	5.0	2.61

The liquid incinerator is air atomized and care must be taken to prevent plugging of the feed lines. Tanks and feed lines are flushed with toluene between burning incompatible liquid wastes. Normal operating temperatures for the liquid incinerator ranges from 1400 to 1600°C.

Each of the two incinerators is followed by a water quench and a cyclone. The quench serves to cool effluent gases. The cyclone acts to remove entrained particulates and droplets prior to scrubbing the exhaust gases.

Gases exiting the two cyclones combine to form a single exhaust stream. The combined gas stream then passes through a three-stage packed tower absorption (scrubber) system for removal of particulates and HCl.

There are two waste streams generated by this incineration facility: scrubber wastewater and ash residue. A portion of the scrubber blowdown (about 10-12,000 gal/hr) is neutralized and processed at an on-site wastewater treatment facility prior to deep well injection. Ash residue is typically allowed to accumulate in the ash sluice and slurry tank for about four weeks. The rotary kiln is shut down approximately once a month for ash removal. Ash is landfilled on-site.

Waste Characterization

During a week-long sampling period, Facility B incinerated the contents of one 20,000 gallon liquid blend tank along with 183 drums representing five different types of solid waste. The solid waste types were: (1) chlorinated hydrocarbon coke from dichlorobutene synthesis, (2) polymeric tar, (3) filtered organometallic waste solids from adiponitrile area, (4) adiponitrile spent filter cartridges, and (5) scrap paint solids. Analytical data summarizing the chemical and physical characteristics of each waste are presented in Table 6.

Toluene is the major volatile organic component of the waste. Several semivolatile compounds were reported in one or more of the waste samples. Copper and nickel are the two metals present at highest concentrations in the liquid waste and they are reported at significant levels in each of the solid wastes as well. Solid waste #5, the scrap paint solids, exhibits the highest metals concentration with high levels of lead, chromium and zinc, three common pigment metals.

The liquid waste blend had a water content of about 17 percent, an organic halide content of 14.24 percent and a fuel value of 11,926 BTU/lb. The fuel value of the solid wastes ranged from 5,866 BTU/lb for the polymeric tar to 12,000 BTU/lb for the scrap paint solids.

Residue Characterization

No volatile or semivolatile organic compounds were found in the ash from Facility B. This ash had a total solids content of about 81 weight percent and a specific gravity of about 1.94. The ash contained nearly 18 weight percent silica. Measurable concentrations of eight toxic metals were reported, with copper (4,600 mg/kg), nickel (4,200 mg/kg) and zinc (1,160 mg/kg) being present at the highest concentrations. Although none of the regulated TCLP metals were found above regulatory level in the TCLP extract, extract levels of copper, nickel and zinc were quite high.

Facility B's scrubber wastewater is very acidic, with pH <1. Four toxic metals - copper, lead, nickel and zinc - are present at concentrations greater than 25 mg/L. No volatile or semivolatile organic compounds were found in the scrubber wastewater.

Table 6. Facility B Waste Characterization*

PARAMETER	Liquid Blend	Solid #1 Chlorinated Hydrocarbon Coke	Solid #2 Polymeric Tar	Solid #3 Filtered Organo-Metallic Waste Solids	Solid #4 Spent Filter Cartridges	Solid #5 Scrap Paint Solids
VOLATILE ORGANICS (ppb)						
Carbon Disulfide	37,000	<62,000	<62,000	<62,000	ND	<62,000
Benzene	47,300	<62,000	<62,000	<62,000	52,000	<62,000
Toluene	340,000,000	10,200,000	<62,000	4,900,000	850	11,700,000
Ethylbenzene	80,300	<62,000	<62,000	72,000	ND	4,600,000
Styrene	181,700	<62,000	<62,000	59,000	ND	<62,000
Xylenes	47,900	<62,000	<62,000	340,000	ND	20,200
4-methyl - 2-pentanone	<10,000	<120,000	<120,000	<120,000	ND	250,000
SEMIVOLATILE ORGANICS (ppb)						
Benzyl Alcohol	1,300,000	<7,500	<60,000	<190,000	ND	<7,500
1,2 dichlorobenzene	1,867,000	<7,500	<60,000	357,000	ND	<7,500
n-nitrosodiphenylamine	3,233,000	<7,500	<60,000	497,000	ND	<7,500
naphthalene	<50,000	<7,500	<60,000	490,000	ND	60,300
2-methylnaphthalene	<50,000	<7,500	<60,000	2,900,000	ND	<7,500
acenaphthene	<50,000	<7,500	<60,000	70,700	ND	<7,500
phenol	<50,000	<7,500	<60,000	<190,000	184,000	<7,500
di-n-butyl phthalate	<50,000	<7,500	<60,000	<190,000	ND	22,300
butyl benzyl phthalate	<50,000	<7,500	<60,000	<190,000	ND	217,000
TOXIC METALS (ppm)						
Antimony	<1	<1	4	116	<1	12
Arsenic	<0.1	<0.1	<0.1	0.21	<0.1	<0.1
Barium	<1	<1	<1	21	4.5	29
Beryllium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cadmium	<0.5	<0.5	<0.5	1.3	<0.5	<0.5
Chromium-hexavalent	0.23	.09	0.26	SI	0.015	0.085

Table 6. (Continued). Facility B Waste Characterization*

PARAMETER	Liquid Blend	Solid #1 Chlorinated Hydrocarbon Coke	Solid #2 Polymeric Tar	Solid #3 Filtered Organo-Metallic Waste Solids	Solid #4 Spent Filter Cartridges	Solid #5 Scrap Paint Solids
Chromium - total	2.2	2.1	0.83	67	10	992
Copper	68	5,700	85	74	1,013	347
Lead	1.7	<1	<1	30	<1	3,470
Mercury	<0.1	<0.1	<0.1	0.9	0.4	<0.1
Nickel	227	91	1.2	500	1,200	39
Selenium	<1	<1	<1	<1	<1	<1
Silver	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Thallium	<1	<1	<1	<1	<1	<1
Zinc	4.8	1.8	1.0	195	60.5	1,670
OTHER ANALYSES						
Wt% Carbon	54.96	48.00	43.12	29.09	IS	50.44
Wt% Hydrogen	8.46	3.61	6.70	6.69	IS	6.45
Wt% Water	17.16	33.91	7.45	27.61	IS	0.52
Wt% Organic Halide	14.24	---	---	---	---	---
Wt% Silica	<0.01	0.77	0.44	15.35	6.99	2.81
Sp. Gravity	0.9576	1.0548	1.2325	1.1313	1.0431	1.1191
Total Solids (mg/kg)	73,000	565,600	659,800	626,033	132,550	604,200
BTU/lb.	11,926	6,243	7,944	5,866	IS	12,000

SI=Sample Interference
IS=Insufficient Sample
* Each value represents the average of three grab samples.

Table 7. Facility B Ash Analytical Data * - Metals

PARAMATER	Compositional (mg/kg)	TCLP Extract (mg/l)	Regulatory Level (mg/l)
TOXIC METALS			
Antimony	14.5	0.03	None
Arsenic	<0.1	0.004	5.0
Barium	75	0.39	100.0
Beryllium	<0.2	0.002	None
Cadmium	<0.5	0.01	1.0
Hexavalent Chromium	0.05	<10	None
Total Chromium	361	0.085	5.0
Copper	4,600	96	None
Lead	340	0.56	5.0
Mercury	1.6	0.004	0.2
Nickel	4,200	34	None
Selenium	<1	<0.05	1.0
Silver	<0.2	<0.005	5.0
Thallium	<1	<0.001	None
Zinc	1,160	25	None
OTHER ANALYSES			
Silica (WT%)	17.77	-	-
Total Solids (mg/kg)	811,000	-	-
Specific Gravity	1.9363	-	-

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* Each Value Represents the Average of Six Grab Samples

Table 8. Facility B Scrubber Wastewater Data*

PARAMETER	Scrubber Wastewater
Toxic Metals (mg/kg)	
Antimony	<1
Arsenic	<0.1
Barium	2
Beryllium	<0.2
Cadmium	<0.5
Chromium-hex	0.2
Chromium-total	1.5
Copper	241
Lead	106
Mercury	<0.1
Nickel	27
Selenium	<1
Silver	<0.2
Thallium	<1
Zinc	363
Other Analyses	
Total Solids (mg/kg)	3867
Total Dissolved Solids (mg/kg)	3500
Total Suspended Solids (mg/kg)	67
Total Organic Halide (wt%)	0.08
Total Chlorine (wt%)	1.59
Specific Gravity (g/mL)	0.9936
pH	0.7

*Each value represents the average of 3 grab samples.

CONCLUSIONS

Because of the limited sampling periods, the data presented in this paper represents only a snapshot of operations at two hazardous waste incineration facilities. It is not known whether this data is typical of normal operation at each of these facilities or of incineration in general.

However, evaluation of the limited data does indicate that significant levels of toxic metals are present in waste solvents and organic process wastes. Since metals are not destroyed by incineration, they tend to concentrate in the treatment residues - ash and scrubber wastewater. Properly designed and operated incineration systems should achieve virtually complete destruction of organic compounds. This appears to be the case at Facility B, where no detectable levels of volatile or semivolatile organics were found in either the ash or scrubber wastewater. Facility A's ash did contain significant concentrations of organic compounds. This may be indicative of incomplete combustion due to inadequate detention time, mixing, or temperature in the incinerator.

WASTE CHARACTERIZATION AND THE GENERATION OF TRANSIENT PUFFS IN A ROTARY KILN INCINERATOR SIMULATOR

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ABSTRACT

The batch introduction of waste-filled drums or containers into rotary kiln incinerators can lead to transient overcharging conditions, which are denoted as "puffs." This paper describes results of an in-house investigation at the U.S. EPA into the waste properties and kiln parameters that determine both the intensity and the magnitude of transient puffs leaving the kiln. The experimental apparatus utilized was a 73 kW (250,000 Btu/hr) laboratory rotary kiln simulator. Surrogate solid wastes in the form of plastic rods and surrogate liquid wastes on corncob sorbent in cardboard containers were investigated. Parametric studies were used to determine the extent to which waste and kiln variables (such as charge mass, charge surface area, charge composition, kiln temperature, and kiln rotation speed) affected the intensity (peak hydrocarbon emission) and magnitude (time-integrated hydrocarbon emission) of puffs.

Results demonstrate the relative ease with which failure conditions are achieved, even at high excess air values and high kiln temperatures. Chemical analysis indicates that puffs arising from even innocuous surrogate wastes can contain numerous hazardous compounds even though adequate DREs (>99.99%) are achieved. Increasing kiln temperature and rotation speed can adversely affect puff intensity, due to increased devolatilization and liquid evaporation rates. There are large effects of waste composition and, for solid wastes, waste surface area is a critical variable.

Stoichiometric oxygen requirement is an important variable distinguishing the transient behavior of different kinds of wastes. Thermogravimetric analyses may be useful in characterizing the propensity of solids to generate transient puffs, while liquid wastes may be best characterized by their normal boiling points and latent heats.

INTRODUCTION

Rotary kiln incinerator systems have been described elsewhere (1,2) and may comprise one of the most versatile waste disposal systems available. Available data (1,3) indicate that these systems are generally safe and effective. However, most data on destruction and removal efficiencies (DREs) of many principal organic hazardous constituents (POHCs) have been obtained under steady-state operating conditions. Little information is available on potential problems during transient conditions that occur when drummed liquids or solid materials are batch fed into the combustion chamber. Overcharging conditions can occur if waste parameters are not properly matched to the incinerator operating conditions. They can lead to heavy loadings of products of incomplete combustion (PICs) in the afterburner and gas cleanup systems. For the sake of brevity, we denote this transient condition as a "puff."

The overall objectives of the current research are to gain engineering insight into potential problem areas related to rotary kiln incineration, with a view to developing predictive methods that correlate possible failure modes to waste characteristics and kiln operating parameters using continuous on-line instrumentation. The specific problem addressed in this paper is that of transient puffs originating from the batch introduction of either solids or liquids on sorbent in containers.

The problem is approached through parametric experimentation on a laboratory-scale rotary kiln incinerator simulator. The value in utilizing a prototype kiln, rather than an actual permitted field device, lies in its ability to allow parametric variation, in a controlled fashion, without loss of the overall complicated salient features of practical kiln operation.

It is hypothesized that a waste parameter of direct importance in the generation of transient puffs is the volatility, or the rate of volatile release, of the waste. When devolatilization occurs rapidly, local oxygen concentrations in the flue gas are almost totally depleted or displaced by the volatilized waste species. A transient puff then moves as a plug through the system. When volatiles are released slowly, however, they are transferred into the flue gas stream without totally depleting the local oxygen levels, allowing more complete oxidation to occur and puffs to be minimized. Therefore, the research results presented here focus primarily on the effects caused by differences in waste volatility. Specifically, we compare results from the batch introduction of surrogate solid wastes, in the form of plastic rods, to those resulting from contained surrogate liquid/sorbent wastes.

LABORATORY ROTARY KILN SIMULATOR

The EPA laboratory-scale rotary kiln simulator was designed to contain the salient features of full-scale kilns, but to remain sufficiently versatile to allow parametric experimentation by varying one parameter at a time, or by controlling a set of parameters independently. A schematic view of the simulator is shown on Figure 1. Its overall characteristics, compared to those of full-scale units, and a detailed description of the hardware specifications have been previously presented (4). The simulator consists of five refractory-lined sections, and is rated at 73 kW (250,000 Btu/hr). The simulator matches the volumetric heat release and gas-phase residence times of full-scale units, but is rated at less than 5 percent of the gross heat input of full-scale units (5).

Surrogate waste materials are batch charged through a sliding gate/ram assembly located on the transition/afterburner section (Figure 1). Quantification of a system upset condition (puff) requires the real-time measurement of system variables. Peak responses of fixed gas and hydrocarbon analyzers indicate extremes. Other useful variables include time-integrated responses; in particular, the time-integrated response of the total volatile hydrocarbon analyzer. This method permits determination of emitted mass. By holding constant sampling temperature, pressure, and flow rate, a constant volumetric flow is delivered to the analyzer's flame ionization detector (FID). Provided the incinerator flue gas flow rate is constant and the gases well mixed, the integrated mass measured is then proportional to the total mass of volatile hydrocarbons passing up the stack during a puff. The peak response, on the other hand, represents the maximum concentration in a puff. The FID is very sensitive to hydrocarbon species but less sensitive to chlorinated compounds.

This paper is concerned only with phenomena occurring in the kiln (primary combustion chamber), so samples withdrawn represent effluent leaving the kiln and entering the afterburner (secondary combustion chamber). Throughout this work, there was neither supplemental heating nor afterburning downstream of the kiln exit. Samples were withdrawn at sample port 4 (Figures 1 and 2). Linak et al. (4) have discussed the extractive sampling and analysis procedures. The results allow determination of the inlet transient conditions with which an afterburner must be capable of dealing, and how these depend on kiln and waste parameters.

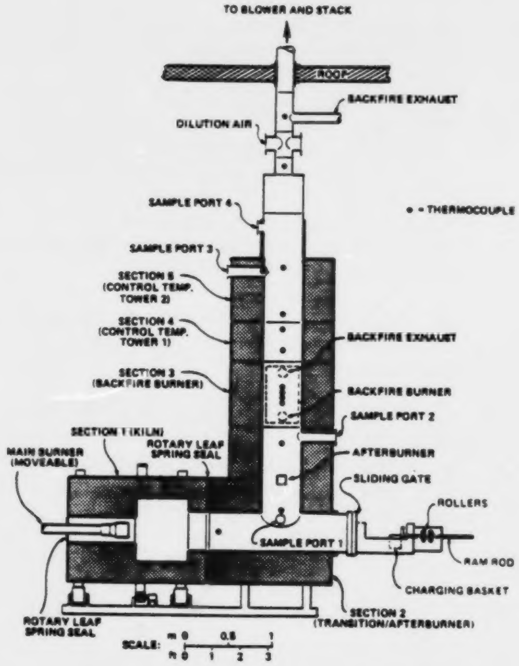
TO BLOWER AND STACK
ROOF
BACKFIRE EXHAUST
DILUTION AIR
SAMPLE PORT 4
• = THERMOCOUPLE
SAMPLE PORT 3
SECTION 5 (CONTROL TEMP. TOWER 2)
SECTION 4 (CONTROL TEMP. TOWER 1)
BACKFIRE EXHAUST
SECTION 3 (BACKFIRE BURNER)
BACKFIRE BURNER
SAMPLE PORT 2
SECTION 1 (KILN)
ROTARY LEAF SPRING SEAL
MAIN BURNER (MOVEABLE)
AFTERBURNER
SLIDING GATE
ROLLERS
SAMPLE PORT 1
RAM ROD
CHARGING BASKET
ROTARY LEAF SPRING SEAL
SECTION 2 (TRANSITION/AFTERBURNER)
SCALE: m 0 0.5 1
ft 0 1 2 3

Figure 1. EPA rotary kiln incinerator simulator.

Figure 2 shows the axial time/temperature profile through the kiln and the subsequent control temperature tower (without additional heat addition) under the low and high firing conditions utilized in the parametric experiments reported in later sections. Gas phase kiln temperatures range from 1258 K (1804 °F) to 1056 K (1440 °F) after 3.6 seconds, and from 1383 K (2030 °F) to 1327 K (1928 °F) after 3.1 seconds under low and high firing conditions, respectively. These gaseous time/temperature profiles simulate full-scale units well.

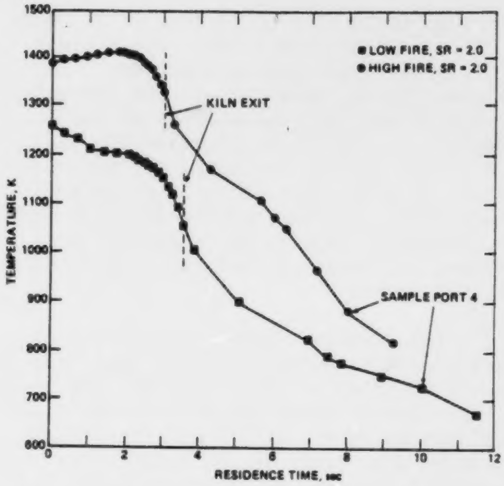

Figure 2. Temperature profile vs residence time, low and high fire test conditions

PARAMETRIC STUDIES

Statistical Design of Experiments

Experimentation was divided into two phases: Phase 1 was concerned with well defined prototype solid plastic wastes; and Phase 2 dealt with liquids absorbed on corncob sorbent in cardboard containers. In both experimental phases, the general methodology employed was that of response surface experimentation (6). This methodology allows one to determine, on the basis of one experiment involving a minimal number of trials, an empirical relationship between the response and the controlled parameters in the experimental region.

For both phases of experimentation, low, intermediate, and high settings of the variables to be investigated were determined. For Phase 1, dealing with prototype solid plastic wastes, these variables were charge mass, charge surface area, and kiln temperature. For Phase 2, which was treated separately and concerned with contained liquid on sorbent wastes, these variables were charge mass, kiln temperature, and kiln rotation speed.

Each phase involved four waste compositions and consisted of at least 24 trials. This allowed quadratic models to be formulated as well as full degree of freedom tests of significance of all main effects and all two-factor interactions (6). Each trial involved between 5 and 15 replicates, depending on the response variance and the availability of waste material. Replicate values of the response variables, including FID measurements of time-resolved total hydrocarbon peak area, and peak height, were averaged. A quadratic response surface model was fitted to these mean values using weighted least squares.

The quadratic model included linear and quadratic dependencies on each independent variable, as well as all the cross-product terms denoting interactions between pairs of variables. The preprogrammed procedures in SAS (Statistical Analysis System), which are relevant to response surface methodology, were used further to interpret the data. Similarities in model coefficients between different wastes (within one phase of experimentation) were statistically tested for evidence that dependencies of the response on various parameters altered from waste to waste. Further tests denoted which linear, quadratic, or interaction dependencies were statistically significant.

Phase 1: Prototype Solid Plastic Wastes

Plastic rods composed of low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and polyvinylchloride (PVC) were chosen as prototype plastic wastes. These rods had well defined initial shapes and allowed, within a certain range, for surface area and mass to be varied independently by varying rod diameters. The plastics span a range of molecular structures, molecular weights, and elemental compositions that are of intrinsic interest to the incineration community because they are widely used and disposed of. In addition to composition, the other independent variables included kiln temperature, charge mass, and charge surface area. The representative kiln temperature used as a control parameter was that measured by a bare type K thermocouple at the kiln exit, 0.97 m (38 in.) from the front burner wall. Low and high fire conditions were used and correspond to the two temperature distributions in Figure 2. The following represent the minimum and maximum values for the parametric test matrix:

(a) Kiln exit temperature, 1105 K (1530°F) minimum, 1339 K (1950 °F) maximum. High fire conditions were obtained by making use of the thermal inertia of the kiln to heat the flue gas to a temperature greater than that occurring naturally at a stoichiometric ratio (SR) of 2.0, as shown in Figure 2.

(b) Charge surface area, 0.050 m^2 (78 - $in.^2$) minimum, 0.095 m^2 (147 $in.^2$) maximum.

(c) Charge mass, 75-100 g (0.17-0.22 lb) (minimum), 500-750 g (1.10-1.65 lb) (maximum). Charge mass was determined by the mass of 6.35, 12.7, and 25.4 mm (0.25, 0.5, and 1.0 in.) diameter rods which produced the proper charge surface area, and was dependent on waste density.

The following kiln operating parameters were kept constant for all runs reported here:

(a) Auxiliary gas flow rate, 5.66 m^3/hr (200 cfh).

(b) Air flow rate, 109.0 m^3/hr (3850 cfh) (leading to constant SR of 2.0 or excess air of 100 percent).

(c) Rotation speed, 1 rpm.

(d) Burner position, -0.34 m (-13.5 in.) inside front burner wall.

(e) Kiln pressure, -37.4 Pa (-0.15 in. H_2O).

(f) Sample port, at position 4 (See Figures 1 and 2).

The area under the transient curve measured by flame ionization detection (FID) is, under constant sampling conditions, proportional to the total quantity of volatile hydrocarbon in a puff. Peak height, on the other hand, represents the instantaneous volatile hydrocarbon concentrations in the puff. The volatile hydrocarbons are defined as those sampled at 420 K (300 °F) and analyzed by continuous FID. Figure 3 shows typical traces for two different plastics at similar test conditions. Clearly there are significant quantitative and qualitative variations in the mechanisms generating transient puffs from solid wastes of differing compositions.

Quadratic models were fitted to the data, using weighted least squares where the weights were equal to the number of

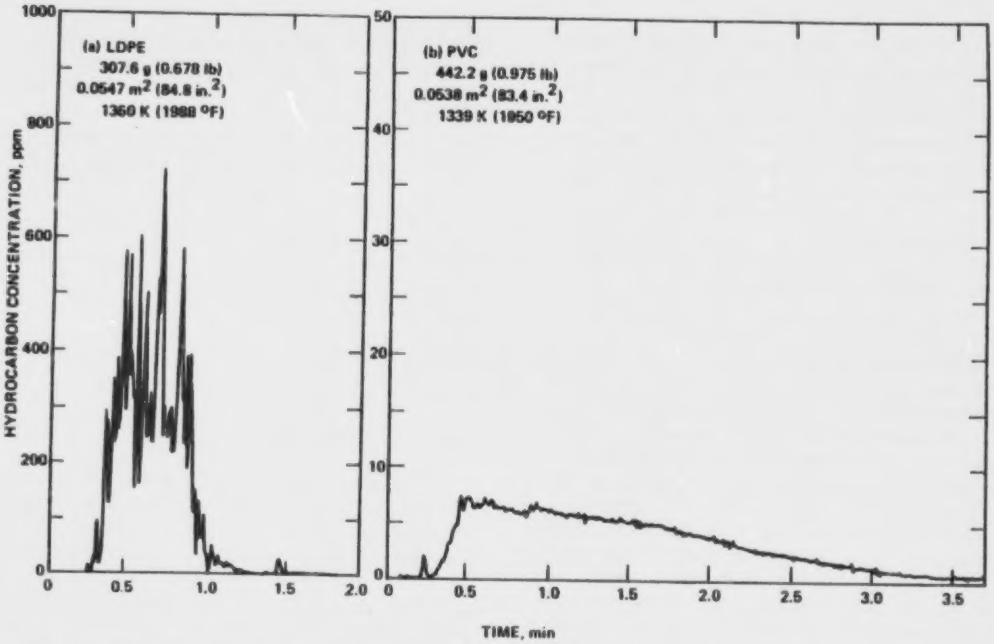

Figure 3. Comparison of LDPE and PVC transient hydrocarbon peak shapes at similar trial conditions.

replicates. These models, obtained using the preprogrammed procedures in SAS, should not be considered unique, since other models might attain fits essentially indentical to those reported here. Once determined, these models can be described pictorially through response surface plots. These contour plots have been presented previously (4) and are not included here.

The final models for peak area accounted for 95.9 percent of the variation in the reponse caused by changes in the controlled variable. The data indicate that, for LDPE, the largest puffs (mass basis) occur at large surface areas and high charge masses. There exists a threshold charge mass, above which puffs rapidly appear, and this threshold is not sensitive to kiln temperature. For LDPE, charge surface area is important and, within a certain charge mass range, can also determine the presence and magnitude of a puff. Increasing kiln temperature decreases the total volatile hydrocarbon species contained in a puff. This significant result was also true for the HDPE, PS, and PVC wastes. PS and PVC wastes, however, showed little effect of surface area on the integrated traces.

Data for maximum peak heights, representing the maximum instantaneous intensity of the puff, were analyzed statistically using the same procedures. The resulting quadratic model accounted for 84.3 percent of the variability of the 37 averaged data points used and is significantly different from the model for peak area. This demonstrates the importance of distinguishing between total mass of the puff and the peak transient concentration. The resulting contour plots for LDPE yield the important result that increasing the kiln temperature increases the maximum instantaneous concentration of volatile hydrocarbons emitted, which is contrary to the school of thought that destruction efficiencies necessarily increase with temperature. Charge surface area is very significant at lower kiln temperature, but less so at higher kiln temperatures. PS and PVC peak heights showed strong surface area effects, but the role of kiln temperature was more ambiguous. For the PVC waste, peak heights were very much smaller, and peak durations very much longer than those for the HDPE and LDPE wastes at similar test conditions (see Figure 3).

It is likely that the formation of puffs from solid plastic wastes is governed by a number of related chemical and physical processes. The stoichiometric oxygen requirement of the plastic waste being incinerated is the most important parameter distinguishing the behavior of different waste compositions. High kiln temperatures enhance rapid devolatilization of the solids, thus increasing the rate of formation of volatile gases to displace or deplete the excess oxygen from the main burner. This may explain the significant effect of kiln temperature on the maximum instantaneous concentration of hydrocarbons in the puff (peak height). It is interesting to note, however, that increasing kiln temperature decreased the total mass of volatile hydrocarbons emitted (peak area). This points to the beneficial (and not unexpected) effects of high temperatures to enhance oxidation mechanisms. Clearly, definition of an optimum condition is not trivial. In practice, afterburners must be able to handle large instantaneous pulses of wastes from the kiln, and so the peak height results are of practical significance.

That surface area appears to be an important parameter, under several conditions, indicates the importance of physical processes, such as heat transfer to the solid and devolatilization from the surface. Decreasing surface area of the solid usually decreased both the intensity of the puff and the total volatile hydrocarbon mass emitted. The exceptions to this occurred at high kiln temperature when heat transfer and subsequent devolatilization are both more rapid.

Heat transfer is clearly not the only important mechanism, since there were vast differences in behavior between waste types. PVC rods had the slowest rate of volatile release, for all surface areas, and therefore always formed the least intense, but longest, puffs. It is expected that their effluent could be handled best by an afterburner. The PE wastes had the most rapid rate of volatile release, and thus are most likely to cause difficulties in the downstream afterburner. This was evident also from thermogravimetric analyses of the solids. These "devolatilization profiles" indicate that, while PVC begins to lose mass at a lower temperature as compared to both LDPE and HDPE, the mass loss rate is slower. Programmed at a temperature ramp of 30 K/min (56 °F/min) in a nitrogen atmosphere, the PVC begins to lose mass at approximately 525 K (486 °F) and is still losing mass at 1175 K (1656 °F). Both LDPE and HDPE, under the same conditions, begin losing mass rapidly at approximately 675 K (756 °F), and essentially all mass is lost by 750 K (891 °F). Clearly, volatile release rates are significant in characterizing the propensity of solid wastes to form transient puffs. The PE wastes had the most rapid rate of volatile release, and thus are most likely to cause difficulties in the downstream afterburner.

Phase 2: Liquid/Sorbent Wastes

In practice, when liquids are incinerated in a batch mode, they are usually held on sorbents in containers or drums. In the research reported here, the containers consisted of 0.947 l (1 qt) closed, cylindrical cardboard vessels, with 135 g (0.298 lb) of shredded agricultural corncob as the sorbent. Prototype liquid wastes included toluene, No. 5 fuel oil, carbon tetrachloride, and methylene chloride. These compounds were chosen because they spanned a range of volatility (the fuel oil, for example, required heating before being absorbed on the sorbent), chemical structure, stoichiometric oxygen requirement, and chlorine substitution.

The experimental design was identical to that used for the prototype solid wastes (Phase 1), except that the variable denoting the solid plastic surface areas was replaced by kiln rotation speed. Rotation speed was chosen because, like surface area for a solid, it directly influences contacting between waste/sorbent and the surroundings. The following represent the minimum and maximum values for the parametric test matrix:

(a) Kiln exit temperature, 1105 K (1530°F) minimum, 1339 K (1950 °F) maximum.
(b) Kiln rotation speed, 0.5 rpm minimum, 2.0 rpm maximum.
(c) Charge mass, 50 g (0.11 lb) minimum, 200 g (0.44 lb) maximum, not including the container and sorbent tare weight of 180 g (0.40 lb).

The other kiln operating parameters were kept constant as described in Phase 1.

Reproducibility was much better for the liquids reported here than for the solids reported in Phase 1. Figure 4 shows typical FID traces for two different liquids at similar test conditions, and again demonstrates the significant quantitative and qualitative variations resulting from charge composition. Nonlinearity of the FID response was observed during the most intense puffs (greater than 10,000 ppm of THC).

Again quadratic models were fitted to the data, using weighted least squares, where the weights were equal to the number of replicates divided by the sample variance between replicates. The final response models for peak area accounted for 99.4 percent variation in the response caused by changes in parameters. Quadratic models for peak heights were very similar to those for peak area, and accounted for 98.9 percent of the variation in the response. In all cases, increasing the kiln rotation speed increased the peak area of the FID hydrocarbon trace and the peak height. This was also true for the two chlorinated liquids. Furthermore, for toluene and fuel oil, both peak area (puff magnitude) and peak height (puff intensity) increased with increasing temperature. This result differs slightly from the solid plastic results, where only puff intensity followed this trend, and it conflicts with the more traditional viewpoint held within the incineration community that high incineration temperatures are always beneficial. This apparent perverse effect of kiln temperature was also observed for methylene chloride, but not for carbon tetrachloride, where results were less definitive.

Contour plots for toluene peak area and peak height exhibited saddle contours when concentrations of volatile hydrocarbons were very high (in excess of 10,000 ppm)(7). These saddle contours are anomalous, and cannot be explained by nonlinear response of the FID. FID response was found to be monotonic with THC concentration up to 40,000 ppm. A possible explanation for the presence of saddles in these plots (7) is that soot formation is disproportionately accelerated at high hydrocarbon loadings and that, therefore, the remaining volatile hydrocarbons measured by the FID are no longer quantitatively representative of total puff size. Saddles did not appear for the less volatile fuel oil where hydrocarbon loadings were significantly lower. Therefore, we believe that, for the less volatile wastes, such as the plastics described above, the FID peak area and peak height contour plots can represent the magnitude and intensity of the puff, provided the hydrocarbon concentrations are not too high.

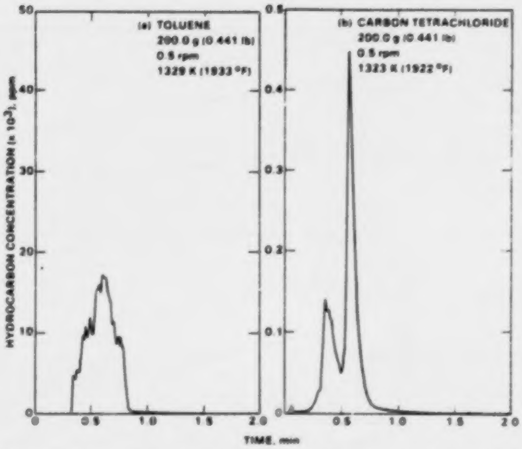

Figure 4. Comparison of toluene and carbon tetrachloride transient hydrocarbon peak shapes at similar trial conditions.

The similarity between contours of integrated measurements (peak area) and those of instantaneous values (peak height) for the liquid wastes (7) suggests that other integrated measurements, such as that of particulate matter trapped on filters during a puff, should also represent trends in both puff magnitude and intensity. Therefore, a statistical analysis was performed on the filter weight recorded for each test. The ensuing model ($r^2 = 0.999$) contained similar terms as the peak area model. Contour plots for toluene and fuel oil, Figure 5, show conclusively that, as kiln temperature is increased, the total soot loading from the kiln to the afterburner is increased; i.e., a much larger puff is formed. This is significant, and once again points to potential failure if the kiln is operated at too high a temperature.

Filter residue mass contour plots for methylene chloride were qualitatively similar to those shown on Figure 5, but

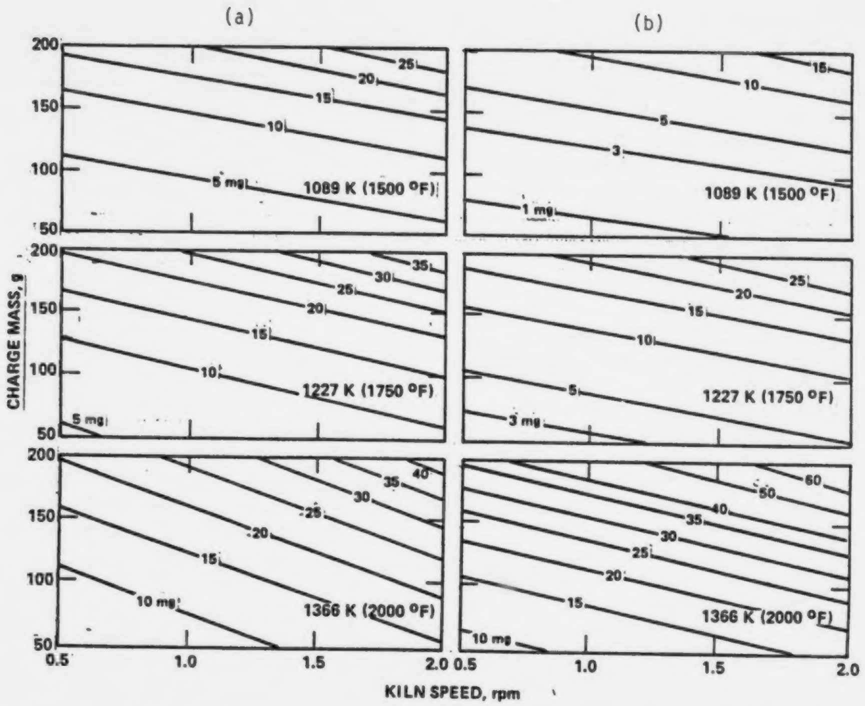

Figure 5. Effect of charge mass, charge surface area, and kiln temperature on (a) toluene and (b) No. 5 fuel oil particulate mass. (Contour values denote filter loadings in milligrams).

indicated only a slight dependence on kiln temperature. Carbon tetrachloride contour plots for both filter residue and peak area differed sharply from those arising from all other liquids, and did not lend themselves to physical interpretation. Furthermore, the carbon tetrachloride filter residues were not black and did not resemble soot while those of the others did. This suggests that, for wastes containing only carbon and chlorine, neither the magnitude nor the intensity of a puff can be determined from measurements of either volatile (FID measureable) hydrocarbons or integrated filter residue mass. Therefore, we explored the value of using CO peak height as an indication of the presence of puffs, since this has been investigated by others (8-15) as a measure of incinerator performance. Statistical analysis of the data describing maximum peak values of CO allowed a quadratic model, similar to that for FID hydrocarbon peak area, to be formulated with an r^2 of 0.988. The resulting CO contour plots for this, and indeed for all other liquids except toluene, were similar to the FID hydrocarbon peak height plots for fuel oil. This suggests that, for fully chlorinated liquid waste compounds, CO may be a useful puff indicator. However, when copious quantities of soot are formed, as for toluene at high kiln temperatures, this indicator ceases to be valid and should not be used alone. It would appear, therefore, that no single indicator of puffs exists for all types of wastes, and that it is desirable always to monitor at least all three indicators used in this work; namely, FID measurable hydrocarbons, CO, and integrated filter residue. For the wastes considered here, however, it was always possible to choose one or more of these indicators such that physically interpretable contour plots resulted.

TRANSIENT PUFF COMPOSITION

Phase 1: Prototype Solid Plastic Wastes

The compositions of the transient puffs from simple polyethylene (PE) and polyvinylchloride (PVC) pipe pieces were determined using VOST and SASS stack sampling trains (16,17), in conjunction with GC-MS analysis (18). These screening tests were used for qualitative identification only since it was not within the scope of this research to perform exhaustive quantitative chemical analyses. Results are presented for a solvent blank and for the test conditions:

(a) A baseline in which the exact procedure for charging was followed, but no charge was entered (i.e., the gate was opened and closed).
(b) One test involving PE pipe with nine charges totalling 2.3 kg.
(c) Two replicate tests (c-1 and c-2), each involving 50 percent PE and 50 percent PVC pipe (by weight), each test consisting of 10 charges totaling 2.7 kg.
(d) One test involving 10 charges of PVC pipe totalling 2.9 kg.

In all cases, the kiln was at high fire conditions (1339 K, 1950 °F) and 100 percent excess air, and the charges were introduced at a rate of one every 10 minutes. The results are shown on Table 1 and were significant in that they showed that hazardous constituents are contained in the puff, and that more diverse organochlorides were detected when the waste consisted of PE/PVC mixtures but not in tests with PVC alone. This is consistent with the transient results described in the preceding sections. PVC alone is devolatilized slowly, and forms small puffs of low intensity and magnitude. PE alone, on the other hand, forms intense puffs of great magnitude, but with no chlorine content. Therefore, the greatest likelihood of hazardous chlorinated hydrocarbons being formed occurs when PE and PVC are mixed. These tests also indicated the presence of trace quantities of penta- through octachloro paradibenzo dioxins (PCDDs) and furans (PCDFs) in several of the samples. These data are presented in Table 2. GC/MS with selected ion monitoring was employed on concentrated samples. No PCDDs or PCDFs were detected from the baseline test (a), the PE test (b), or the solvent blank. Both PE/PVC tests (c-1 and c-2) indicated the presence of several of these compounds but only the second test (c-2) was quantified. The PVC test (d) indicated the presence of octa-CDF. Again, these results are consistant with proposed mechanisms regarding puff formation.

Phase 2: Liquid/Sorbent Wastes

As in Phase 1, compositions of the transient puffs from the liquid wastes were determined using VOST and SASS stack sampling trains in conjunction with GC/MS analysis. The ability of the kiln alone to produce PICs and, additionally, its ability adequately to destroy the POHC species, were examined. Results are presented for a solvent blank and for the following test conditions:

(a) A baseline in which the exact procedure for charging was followed, but no charge was entered (i.e., the gate was opened and closed).
(b) A sorbent/container blank (10 charges totaling 1.8 kg).
(c) Two replicate tests (c-1 and c-2), each involving 10 charges of toluene alone totaling 3.8 kg (including 1.8 kg of sorbent and container).
(d) Two replicate tests (d-1 and d-2), of 50 percent toluene and 50 percent carbon tetrachloride (by weight), each test consisting of 10 charges totaling 3.8 kg (including 1.8 kg of sorbent and container).
(e) One test involving 10 charges of carbon tetrachloride totaling 3.8 kg (including 1.8 kg of sorbent and container).

As in Phase 1, the kiln was operated at high fire conditions (1339 K, 1950°F), 100 percent excess air, and the charges were introduced at a rate of one every 10 minutes. The VOST results show benzene and toluene to be present for all of the tests including the baseline test (a), and carbon tetrachloride to be present in both the toluene/carbon tetrachloride (d-1 and d-2) and carbon tetrachloride (e) tests. DRE calculations, however, indicate adequate destruction of the POHC species in excess of 99.99 percent. Particulate loadings, however, determined by SASS filter weights averaged over the entire 100 minute test, exceeded the RCRA regulated limit of 180 mg/dscm (0.08

Table 1. Selected RCRA Appendix VIII compounds identified in test burns charging polyethylene and polyvinylchloride pipe.[1]

	Solvent Blank	Baseline[2] (a)	PE (b)	PE/PVC[3] (c-1)	PE/PVC[3] (c-2)	PVC (d)
(2-Ethylhexyl)phthalate		X	X	X	X	X
Naphthalene		X	X	X	X	X
Dichlorobenzene				X	X	X
1,2,4-Trichlorobenzene				X	X	
Hexachlorobenzene				X	X	
Pentachlorophenol				X	X	
Fluoranthene			X			

[1] In all cases, the kiln was at high fire conditions (1339 K, 1950 °F), 100 percent excess air (SR=2.0), 1 rpm kiln rotation, and 9 to 10 charges, averaging 270 g each, were charged one every 10 minutes.

[2] Baseline test sampled auxiliary fuel combustion gas products; no waste material charged.

[3] PE/PVC mixed charges were 50 percent each by weight.

Table 2. PCDD and PCDF flue gas concentrations determined from test burns charging polyethylene and polyvinylchloride pipe.

Average flue gas concentration, ppt (volume).

	Solvent Blank	Baseline (a)	PE (b)	PE/PVC (c-1)	PE/PVC (c-2)	PVC (d)
Mono-CDD					-[1]	-
Di-CDD					-	-
Tri-CDD	N	N	N	D N	-	-
Tetra-CDD	O	O	O	E O	5.4	-
Penta-CDD	N	N	N	T T	3.4	-
Hexa-CDD	E	E	E	E	-	-
Hepta-CDD				C Q	18.4	-
Octa-CDD				T U	13.4	-
				E A		
Mono-CDF	D	D	D	D N	-	-
Di-CDF	E	E	E	T	-	-
Tri-CDF	T	T	T	I	-	-
Tetra-CDF	E	E	E	F	20.1	-
Penta-CDF	C	C	C	I	-	-
Hexa-CDF	T	T	T	E	58.1	-
Hepta-CDF	E	E	E	D	62.8	-
Octa-CDF	D	D	D		27.2	10.9

[1]- Not detected

gr/dscf, corrected to 7 percent O_2) (19) for all samples except the baseline (a), sorbent/container blank (b), and carbon tetrachloride (e) experiments. The toluene (c-1 and c-2) and toluene/carbon tetrachloride (d-1 and d-2) tests exceeded the particulate limit by as much as a factor of nine.

Extracted and concentrated samples from all parts of the SASS train were combined. Table 3 presents a selected list of major peaks identified by GC/MS analysis. The data show contaminant phthalate ester and chlorocyclohexanol species present in all the samples, including the baseline (a) and sorbent/container blank (b). Of interest is the detection of several polycylic aromatic hydrocarbon (PAH) compounds (acenaphthalene, anthracene, fluoranthene, and pyrene) in the toluene samples (c-1 and c-2), but not in the toluene/carbon tetrachloride (d-1 and d-2) or carbon tetrachloride (e) samples. In addition, low concentrations of tetra- and pentachlorobenzene were detected in the toluene/carbon tetrachloride samples (d-1 and d-2), but not in any of the other samples. The carbon tetrachloride (e) sample was found to be free of both the chlorinated benzene and PAH compounds. Again these results are consistent with the transient results presented in the previous sections of this paper and with the analytical results from Phase 1.

Samples were also analyzed for PCDDs and PCDFs. Again, GC/MS with selected ion monitoring was employed on concentrated samples. Table 4 summarizes the integrated concentrations of PCDD and PCDF species identified in these flue gas samples. No PCDDs or PCDFs were detected in the solvent blank, baseline (a), sorbent/container blank (b), or toluene (c-1 and c-2) samples. Both the toluene/carbon tetrachloride mix (d-1 and d-2) and the carbon tetrachloride (e) samples contain parts per trillion concentrations of tetra- through octachloro dioxins and furans. The carbon tetrachloride sample (e) contained substantially less PCDDs

Table 3. Selected compounds identified in test burns charging toluene and carbon tetrachloride.[1]

	Solvent Blank	Baseline (a)[3]	Sorbent/ Container Blank (b)	Toluene (c-1)	Toluene (c-2)	Toluene/ Carbon Tetrachloride (d-1)[4]	Toluene/ Carbon Tetrachloride (d-2)[4]	Carbon Tetrachloride (e)
Chlorocyclohexanol	X	X	X	X	X	X	X	X
Phthalate ester	X	X	X	X		X	X	X
Tetrachlorobenzene[2]						X	X	
Pentachlorobenzene[2]						X	X	
Naphthalene				X	X			
Acenaphthalene				X	X			
Anthracene				X	X			
Fluoranthene				X	X			
Pyrene				X	X			

[1] In all cases, the kiln was at high fire conditions (1339 K, 1950 °F), 100 percent excess air (SR=2.0), 0.5 rpm kiln rotation, and 10 charges of 380 g (0.84 lb) each (including 180 g, 0.40 lb, container/sorbent), were charge one every 10 minutes. Trace quantities of varying chlorinated compounds were identifed in all samples including baseline, sorbent/container blank, and toluene samples.

[2] Present in low concentrations in comparison to others listed, but not identified in any other sample.

[3] Baseline test sampled auxiliary fuel combustion gas products; no waste material charged.

[4] Toluene/carbon tetrachloride charges were 50 percent each by weight.

and PCDFs than did the toluene/carbon tetrachloride mix samples (d-1 and d-2) in comparison. However, it must be restated that all these samples represent effluent from the kiln prior to the afterburner, and therefore describe what must be destroyed by the afterburner or removed downstream.

DISCUSSION

A significant distinguishing property of both solid and liquid waste, regarding the generation of puffs, is its stoichiometric oxygen requirement. However, other fundamental mechanisms governing the generation of puffs for plastic wastes are different than those for liquid wastes on sorbents. For the former, the volatile release rate depended on the rate of pyrolysis of the plastic, and this could be correlated with differential thermogravimetric analyses. For liquid wastes on sorbents, thermogravimetric analysis showed no interesting distinguishing features between wastes and therefore could not be related to the contour plots describing the transients. Rather, the volatile release rate is most probably controlled by heat transfer to (and simple evaporation from) the sorbent, and the surface exposure of the sorbent to the surroundings. If this hypothesis is correct, then the important waste parameters for liquid wastes would be their normal boiling points and their latent heats of vaporization. One might further hypothesize that surface exposure of the sorbent is increased as kiln rotation speed is increased. This hypothesis is consistent with all the data presented here, which indicate that both puff magnitude and intensity increase with increasing kiln rotational speed. Work is in progress to test these hypotheses using phenomenological models.

Time resolved measurement of puffs is not trivial. Volatile hydrocarbons give a fair indication when levels are not too high (e.g., at low to moderate volatile release rates), as for fuel oil or plastics. Filter residue mass was a better indicator for toluene, when black particulate matter appeared to be the prime constituent of a puff. Neither of the above was suitable for carbon tetrachloride waste, for which CO appeared to be the better on-line indicator. However, CO was a poor indicator for toluene. Therefore, we conclude that no single on-line measurement is suitable for all liquid wastes, and that the omission of any one of the indicators used here might lead to error. However, simultaneous

Table 4. PCDD and PCDF flue gas concentrations determined from test burns charging toluene and carbon tetrachloride.

Average flue gas concentration, ppt (volume).

	Solvent Blank	Baseline (a)	Sorbent/ Container Blank (b)	Toluene (c-1)	Toluene (c-2)	Toluene/ Carbon Tetrachloride (d-1)	Toluene/ Carbon Tetrachloride (d-2)	Carbon Tetrachloride (e)
Mono-CDD						-[1]	-	-
Di-CDD						-	-	-
Tri-CDD	N	N	N	N	N	-	-	-
Tetra-CDD	O	O	O	O	O	1.3	1.8	0.9
Penta-CDD	N	N	N	N	N	1.3	2.5	-
Hexa-CDD	E	E	E	E	E	0.8	1.7	-
Hepta-CDD						-	0.7	-
Octa-CDD						-	0.2	0.6
Mono-CDF	D	D	D	D	D	-	-	-
Di-CDF	E	E	E	E	E	-	-	-
Tri-CDF	T	T	T	T	T	-	-	-
Tetra-CDF	E	E	E	E	E	14.1	8.4	0.9
Penta-CDF	C	C	C	C	C	16.9	21.5	0.7
Hexa-CDF	T	T	T	T	T	7.7	12.9	0.7
Hepta-CDF	E	E	E	E	E	1.2	2.5	0.8
Octa-CDF	D	D	D	D	D	-	0.2	1.8

[1] - Not detected

measurements of volatile hydrocarbon concentration, filter residue mass, CO, CO_2, O_2, and NO_x as puff indicators appear to span the waste conditions encountered in this study.

Puffs consist of toxic secondary combustion products (PICs). Chlorinated PIC compounds are more likely to be formed when mixtures of dissimilar materials, such as PE and PVC or toluene and carbon tetrachloride, are burned, than when PVC or carbon tetrachloride are burned alone. PVC or carbon tetrachloride form relatively small puffs. Excess oxygen is neither totally depleted nor displaced, and even though large quantities of chlorine are present, few chlorinated PICs are formed. PE or toluene alone, on the other hand (toluene is a known soot precursor), form intense puffs of great magnitude. Excess oxygen is much more extensively depleted or displaced, and although no chlorine is present to allow the formation of chlorinated PICs, there is a propensity to form large quantities of soot and associated PAH compounds. PE/PVC or toluene/carbon tetrachloride mixtures provide both the necessary chlorine and pyrolytic conditions to promote chlorinated PICs. Therefore, carbon tetrachloride alone may not be the most suitable surrogate compound to investigate the formation of PICs, at least in the transient mode.

Finally, the thermodynamic stability of certain chlorinated compounds, including TCDD [thermochemistry from Tsang and Shaub (20)], was investigated for a wide range of local stoichiometries likely to be valid in the puff. Multicomponent equilibrium calculations, involving 33 species, indicated that very fuel-rich conditions possibly encountered in the puff could create thermodynamically stable trace quantities of CH_2Cl_2, CH_3Cl, and COCl but that predicted TCDD mole fractions were always less than 10^{-19}. The levels of TCDD compounds measured in this work are above equilibrium concentrations for all possible conditions in the puff; therefore, their formation is likely to be kinetically, rather than equilibrium, controlled.

CONCLUSIONS

A laboratory rotary kiln simulator can yield useful insight into factors influencing the formation of transient puffs caused by the batch introduction of both solid and liquid wastes. The data suggest that the volatility of the waste, or rather, the rate of volatile matter release, is of paramount importance in determining the occurrence of puffs. There are therefore large differences between solid and liquid wastes, and more volatile substances yield larger puffs more readily. These transients can be minimized at lower kiln temperatures, which is contrary to normal practice. Devolatilization of the waste, however, was visually observed to depend on many physical events occurring in the kiln, including, but not limited to, the way in which the waste contacted both the kiln walls and the flue gas from the main burner.

Transient puffs can be easily generated in the kiln and contain hazardous substances even from quite innocuous compounds such as polyethylene and polyvinylchloride. DREs calculated for liquid wastes were greater than 99.99 percent. Mixtures of wastes can lead to more diverse hazardous substances than wastes incinerated individually.

The most significant implication for practical systems is that the afterburner plays an essential role in preventing transient puffs from both solid and liquid wastes from entering the environment. Great care must be taken in the afterburner design to ensure that the puff components are properly oxidized and destroyed. Future work could be directed at ensuring that the kiln performs more efficiently as a thermal oxidizer rather than merely as a pyrolysis furnace. This work suggests that this is not to be achieved simply by operating at high excess air, at high temperatures, and with good contacting. In fact, for the latter two variables, the converse may be true.

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ON-LINE MONITORING OF ORGANIC EMISSIONS WITH A MOBILE LABORATORY

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ABSTRACT

EPA's Hazardous Air Pollutants Mobile Laboratory (HAPML) was designed as an integrated sampling and analytical package for real-time monitoring of combustion sources. The HAPML is equipped with organic and inorganic analytical equipment and is completely housed in an 8 m long van.

The HAPML recently participated in a total mass emissions test at a full scale rotary kiln incinerator. The complete field test was conducted by EPA's Hazardous Waste Engineering Research Laboratory under the direction of Robert C. Thirnau and will be reported separately. The HAPML collected continuous emission monitor (CEM), gas chromatograph/flame ionization detector (GC/FID), and GC/mass spectrometry (MS) data during steady state conditions and upsets which simulated conditions which might occur in normal operation. The GC/FID was used for on-line analysis of light hydrocarbons. The volatile organic sampling train (VOST) was used to collect samples for analysis by the GC/MS to identify other organic compounds in the stack gas. CO, CO_2, O_2, and NO_x data were collected with the CEMs.

This paper will discuss the data collected during the field test and other capabilities of the HAPML. Future plans include exploring those other capabilities which include using the MS as a single ion monitor and testing the HCl monitor.

INTRODUCTION

Because of the interest in determining the performance of an incinerator on a real-time basis and the need to characterize the emissions from a variety of incinerators, EPA initiated a project to build a mobile laboratory for continuous monitoring of emissions and operating parameters of hazardous waste incinerators. The objective of this project was to provide an integrated sampling and analytical package for evaluation and development of continuous and semicontinuous monitors for hazardous waste incinerators. The result of the project is the Hazardous Air Pollutants Mobile Laboratory (HAPML), designed to be easily transported for use by research projects at a variety of incinerators.

This paper will discuss the development of the HAPML, its capabilities, data obtained while monitoring a hazardous waste incinerator, and future plans.

DEVELOPMENT OF THE HAZARDOUS AIR POLLUTANTS MOBILE LABORATORY

The HAPML was constructed as an

integrated sampling and analytical package for use in hazardous waste incineration research. The HAPML utilizes extractive sampling technology, and all components are housed in a standard 8 m long, self-propelled van.

The HAPML contains continuous monitors for real-time analysis of CO, CO_2, NO_x, O_2, SO_2, and HCl. Organic analytical instrumentation includes a gas chromatograph (GC) equipped with a flame ionization detector (FID), and a mass spectrometer (MS). The layout inside the van is shown in Figure 1.

The sampling system delivers a portion of the gaseous effluent in the stack to the HAPML while maintaining sample integrity. Major considerations in on-line analysis include the interferences caused by particulates and moisture and minimizing reactions and interactions in the sample line.

All particulates must be removed from the sample stream because of problems they may cause in the analytical instrumentation: plugging of the lines, damage to the optical system, or light scatter resulting in erroneous data. The HAPML uses a particulate removal system located 3 m from the stack sampling port. The particulate removal system is housed in a heated aluminum filter box and consists of a high surface area, low pressure drop, spun glass-wool filter. Valves located in this box allow calibration gases to be sent from the van, through the sampling system, back to the van, and into the appropriate analytical instrument for system checks.

Water, a natural combustion product, may condense in the analyzers or can result in optical interferences. The problems may be handled in different ways depending on the species of interest. The stack gas emissions flowing to the CO, CO_2, O_2, and NO_x monitors are cooled and dried using a condenser and a Perma-Pure dryer. NO_2 is soluble in water. However, since NO_x is typically about 95% NO, the loss is negligible. Since SO_2 and HCl are also soluble in water, these gases would be removed along with the water. Therefore, these problems must be resolved with a different procedure. A sample conditioner is used to dilute these gas streams with dry, clean air to minimize the interference effects of water vapor.

Considerations in temperature and material are required to ensure that reactions in the sample line do not occur. A Teflon line, heated to approximately 150°C, is used to transport the sample from the stack into the HAPML. This limits the on-line organic analysis to those compounds with boiling points less than the temperature of the sample line. Many species of interest lie outside this range and may not be monitored in this fashion. Care must be taken to eliminate any cool spots in the line, such as at fittings. If any chlorine is in the system, stainless steel connections can react with the sample and must be removed. Teflon fittings or stainless steel fittings lined with Teflon, which eliminates contact between the stainless steel and the sample, must be used.

The organic analytical system was designed to provide information in a variety of ways. The sampling system may be used to deliver sample gas: directly to the GC/MS or the GC/FID for semicontinuous monitoring, to the MS for on-line analysis of selected organic compounds, or to the FID for total hydrocarbon (THC) concentration determination. The HAPML may also be used as an on-site laboratory for volatile organic analysis. It is equipped with a Volatile Organic Sampling Train (VOST) for collection and concentration of the gas effluent if the compounds of interest are present below the detection limits of the analytical instrumentation (1). These samples may be analyzed on the GC/MS or the GC/FID using a NuTech purge and trap system with a clamshell oven for thermal desorption. The purge and trap unit is equipped with a Tekmar sparger tube assembly. A quick analysis may be invaluable in determining the amount of stack gas to be concentrated to provide the proper amount of sample for more extensive analytical procedures. Also, organics collected on a sorbent material may be suspected of reacting, partially desorbing, or becoming contaminated if they are not stored properly or if they are not analyzed quickly enough. Therefore, analyzing the samples on-site improves the reliability of the results.

A two column option has recently been added to the GC to allow simultaneous operation of the GC/MS and the GC/FID. VOST samples may be analyzed on the GC/MS while the GC/FID is used for semicontinuous monitoring of selected compounds or vice versa. The only limitation is the temperature of the oven. It may be operated isothermally or, if a temperature program is used, the runs for the GC/FID and the GC/MS must be started simultaneously.

Standard gases traceable to the National Bureau of Standards (NBS) are used to calibrate the continuous emission monitors (CEMs) for quantitative analysis. Onboard storage is available for gas cylinders. A zero calibration (typically nitrogen gas) and standards in two concentrations are used each day of sampling to calibrate the instruments. The zero and the standard closer to the concentration seen while sampling are checked during the middle and at the end of the sampling period. If analyzed concentrations of these gases fall outside specified limits, the instruments are recalibrated. The values from the calibration checks are used to determine the precision and accuracy of the instruments.

The organic system is calibrated similarly, although the standards vary. When VOST analyses are being done, organic liquids are injected onto VOST cartridges, desorbed, and analyzed according to the VOST protocol. Standard gases for common organic classes are sometimes used, as well as liquids injected directly into the GC. The HAPML is also equipped with a permeation chamber for calibration of the organic system and the HCl monitor. Most analysis done with the organic system is qualitative and semi-quantitative. Precision and accuracy of the instruments are determined similarly to the CEMs.

All MS and CEM data are acquired by two onboard computers (a DEC PDP 11 and a Compaq Deskpro 286). FID data are acquired using an HP 3393A integrator. Backup of data collected is provided by strip chart recorders for the CEMs and a tape backup in the Compaq computer.

TOTAL MASS EMISSIONS (TME) TEST

Field tests conducted by the Hazardous Waste Engineering Research Laboratory (HWERL) indicate that most facilities achieve high DREs (2). However, both the studies and the EPA's Science Advisory Board's later review raised additional questions about the performance of hazardous waste incinerators. A major concern is the unidentified emissions, both compounds referred to in Appendix VIII of the Solid Waste Methods 846 (SW846) as well as those not listed that are formed in the combustion process. The concerns expressed are not limited to simply stack emissions, but all other posssible effluents. These include organics, trace metals, and other chemicals associated with incinerator ash, spent water, and particulates. Because of this concern, HWERL initiated a project to quantify the total mass emissions (TME) from a commercial incinerator. HWERL had complete responsibility for the TME test, under the direction of Robert C. Thurnau. Services of the HAPML were requested to provide CEM and on-line GC/FID data. The opportunity also allowed for further evaluation of the capabilities of the HAPML in field conditions.

The TME project was conducted at a full scale, industrial rotary kiln incinerator. Two sets of triplicate 2 hour tests were scheduled. One set was performed under steady state conditions similar to those used for a trial burn. The second set of tests was conducted under transient conditions which included variations in the process similar to those expected during routine incinerator operations.

The process tested is a multiple stream hazardous waste incinerator with a horizontal rotary kiln, secondary combustion chamber, and wet scrubber. Waste feed streams consist of the solid waste to the kiln and a liquid mixture of organic and aqueous waste to the secondary chamber and the kiln.

During this study, three types of solid waste were fed to the kiln: alternate drums containing hydroxypropylmethyl cellulose, polyethylene wax or powder, and chlorinated pyridine tar were fed into the kiln at a rate of 20 bbl/hr (3200 l/hr). The waste drums began feeding into the kiln about 30 min prior to the beginning of each test period to compensate for the 30 to 60 min kiln residence time.

A single liquid organic tank was prepared with a 5% spike of carbon tetrachloride. The tank was continuously agitated to preserve homogeneity. The plant fired other wastes until the sampling crews were ready and then switched to the spiked waste. Sampling took place during this period. During the steady state tests, the liquid waste was fed into the kiln and the secondary chamber at about 2 gpm (7.6 lpm). This feed rate was increased by fully opening the control valve for 7 sec approximately every 30 min to simulate transient conditions.

HAPML TME RESULTS

CEM data were acquired every 5 sec and recorded in 30 sec averages. Table 1 lists the average concentrations for the six tests for O_2, CO_2, and CO. Tests 1 through 3 are steady state tests, while 4 through 6 are transient tests. The triplicate steady state runs show very good reproducibility. The O_2 varied from 8.1 to 8.9%, the CO_2 from 6.3 to 6.4%, and the CO from 0 to 1 ppm.

Although an effort was made to achieve reproducibility for the transient tests as well, the results show a fairly wide range of values resulting from the three tests. In all cases, the peak shape for the CO concentration resulting from the induced upset and corresponding increase in CO concentration was similar. The peak maximum occurred about 1 min after the initial increase in CO concentration and did not decrease to the normal level until about 3 min after first rising above the standard concentration. The minimum level of O_2 and the maximum level of CO_2 occurred simultaneously during the transient condition. The CO_2 and O_2 appeared consistently as mirror images of the other. There is little difference between the two types of tests in the O_2 and CO_2, and the transient conditions are not obvious. The relationship between the time of occurrence for the extremes of the O_2 and CO_2 concentrations and the maximum in the CO concentration varied.

The GC/FID was used for on-line monitoring of low molecular weight hydrocarbons. Only methane and ethylene were detected. Table 2 gives the results. Averages of all readings for the steady state tests are given. Two averages are given for each of the transient tests. The data which occurred between the transient conditions are given under steady state, and the data acquired during the transient conditions (when CO maxima were apparent) are listed under transient. Ethylene was detected only during the transient tests and, except in one instance, occurred simultaneously with the transient condition.

Test 4 shows an obvious difference between the methane concentrations occurring between and at transient conditions, as expected. Tests 5 and 6 do not exhibit this behavior. A Mann-Whitney Two-Sample Test was performed on the methane data to determine if the two sets of numbers could have occurred purely by chance; i.e., that there was no real difference between the two. A Kendall's Rank Correlation was performed to determine if there was a correlation between the methane data and the CO level. Table 3 summarizes the results. The larger numbers indicate a greater probability that any difference between the methane values or any correlation with CO is purely chance. The low numbers for Test 4 indicate that there is a real difference between the two sets of methane data in that test and that there is a good correlation between the methane and CO concentrations. The unexpected results of Tests 5 and 6 could possibly be explained by some other upset in the system that damped out the effect of the induced upset.

VOST samples were taken to determine if any volatile organics were present below the detection limit of the instrument. The major peak detected could not be identified. The next two peaks in order of intensity were benzene and toluene. Benzene averaged 13 ppb for the steady state tests. Figure 2 compares the benzene concentration of the transient tests, after subtracting the background or steady state level, with the peak maximum of the CO concentration which occurred during the VOST run. Although data are limited, Figure 2 suggests that, while CO may not be a good indicator of DRE (3), the CO level may be related to the concentrations of at least some PICs. Each data point represents only one VOST analysis. No change was seen in the toluene concentration between the steady state and transient tests. It remained at 2 or 3 ppb for all tests.

CONCLUSIONS

The results of the field test indicate that the HAPML can be successfully operated in the field and produce quality data. The HAPML was audited during the field trip discussed in this paper and was found to be acceptable with minor recommendations. All recommendations have since been implemented.

Several problems in the MS have since been identified, and steps have been taken to correct them. These include an update of all software, improvement of the library search capabilities, and making the single ion monitoring capability operational. It is hopeful that the MS, in the single ion monitoring mode, can be used as a continuous monitor for PICs. There is, without question, a need for real-time measurement capability for hazardous waste incinerators. The HAPML provides a means of testing a number of incinerators and can be used to characterize the volatile organics and permanent gas emissions.

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TABLE 1. CEM RESULTS

Test No.	O_2 (%)	CO_2 (%)	CO (ppm)
1	8.9	6.3	1.0
2	8.1	6.4	0.0
3	8.6	6.3	0.1
4	8.2	6.2	9.0
5	8.7	6.3	11.7
6	10.3	5.2	14.3

TABLE 2. RESULTS OF ON-LINE GC/FID MONITORING

Test No.	Steady State		Transient	
	Methane (ppm)	Ethylene (ppm)	Methane (ppm)	Ethylene (ppm)
1	1.7	ND	NA	NA
2	1.1	ND	NA	NA
3	1.0	ND	NA	NA
4	1.9	0.8	11.0	1.7
5	93.2	ND	92.9	1.3
6	48.3	ND	52.6	0.3

ND = Not detected
NA = Not applicable

TABLE 3. SUMMARY OF STATISTICAL ANALYSIS

Test No.	Probability	
	Mann-Whitney	Kendall
4	0.036	0.005
5	0.421	0.364
6	0.238	0.168

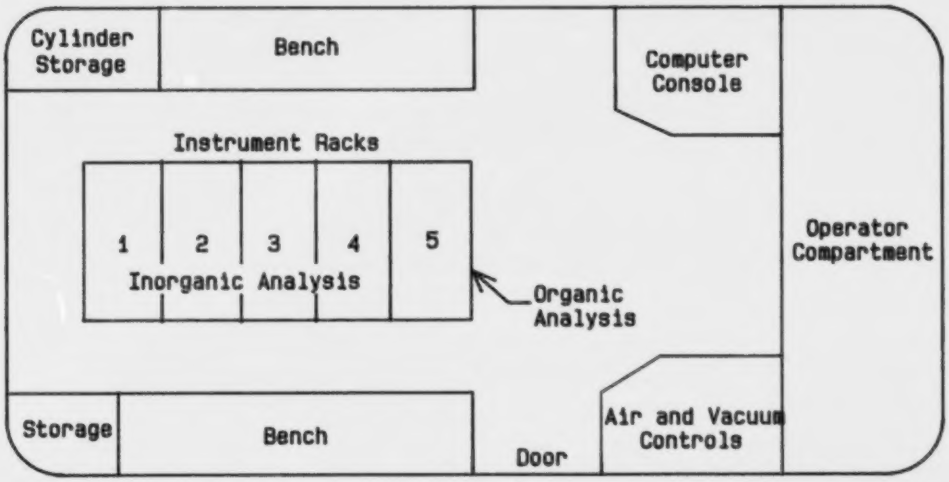
Cylinder Storage
Bench
Computer Console
Instrument Racks
1
2
3
4
5
Inorganic Analysis
Organic Analysis
Operator Compartment
Storage
Bench
Door
Air and Vacuum Controls

Figure 1. HAPML floor plan.

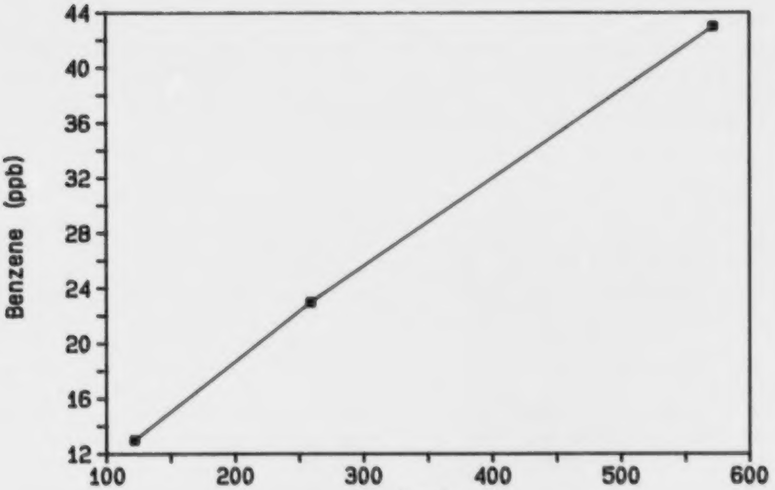

Figure 2. Comparison of benzene concentration and maximum CO concentration.

TOTAL MASS EMISSIONS FROM A HAZARDOUS WASTE INCINERATOR

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ABSTRACT

Past studies of hazardous waste incinerators by the Hazardous Waste Engineering Research Laboratory have primarily examined the performance of combustion systems relative to the destruction and removal efficiency (DRE) for Resource Conservation and Recovery Act (RCRA) Appendix VIII compounds in the waste feed. These earlier studies demonstrated that in general most facilities performed quite well relative to the DRE. However, subsequent review by the Environmental Protection Agency's (EPA) Science Advisory Board raised questions about additional Appendix VIII or non-Appendix VIII constituents that were not identified in the earlier tests and might be emitted from hazardous waste combustion. This paper presents results of a characterization of incinerator effluents to the extent that the emitted compounds can be identified and quantified. Measurements were made of both Appendix VIII and non-Appendix VIII compounds in all effluents (stack, ash, water, etc.) from a full scale incinerator. A broad array of sampling and analysis techniques were used. Sampling methods included Modified Method 5, volatile organic sampling train (VOST), and specific techniques for compounds such as formaldehyde. Analysis techniques included gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Continuous measurements were also made for a variety of compounds including total hydrocarbons by flame ionization detector (FID).

INTRODUCTION

A common theme in literature and religion dealt with the idea that the trials and tribulations experienced in life are a form of punishment resulting from our ancestor's sins. The problems of toxic and hazardous wastes can be compared with this concept in that we are now faced with the cleanup of hundreds of old disposal sites that now threaten the health and well-being of thousands of citizens. Coupled with the cleanup effort is the idea that toxic and hazardous wastes generated today will now be disposed of in an environmentally safe manner so as not to be a problem to future generations. As a public expression of commitment to cleaning up existing hazardous waste sites, the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) legislation and its reauthorization Superfund Amendments Reauthorization Act (SARA) were enacted. To handle the present day problems of toxic and hazardous waste disposal, the RCRA was enacted in 1976 and amended in 1984 by the Hazardous and Solid Waste Amendments (HSWA). Commensurate with these statutes, the EPA regards incineration as one of the principal technology candidates for the ultimate safe disposal of wastes and promulgated the following standards in the Federal Register, Volume 46, No. 15, on January 23, 1981.

1. An incinerator must achieve a DRE of 99.99 percent for each principal organic hazardous constituent (POHC) designated for each waste feed.

2. An incinerator burning hazardous waste must not emit more than 1.8 kilogram/hour (kg/hr) of hydrogen chloride (HCl) or must remove 99 percent of the hydrogen chloride from the exhaust gas.

3. An incinerator burning hazardous waste must not emit particulate matter exceeding 180 milligrams per dry standard cubic meter (mg/dscm).

The above standards only address the POHC residues at the stack and fail to address other possible effluents such as products of incomplete combustion (PICs) associated with stack gases, and POHC residues, trace metals, and other chemicals associated with incinerator ash, spent water, and particulates. Because these effluents may be equally or more hazardous than POHCs themselves, research is needed to qualitatively and quantitatively study the characteristics of all possible effluents and to provide engineering data for regulatory support.

To meet this need, Midwest Research Institute (MRI) was contracted by the Hazardous Waste Engineering Research Laboratory (HWERL), EPA, Cincinnati, Ohio, to conduct an inventory of a hazardous waste incinerator in which the total mass emissions (TME) were measured and quantitated to the best extent possible. This paper presents preliminary results from this study.

APPROACH

This study addressed two primary objectives. First, a wide array of sampling and analysis (S&A) techniques were used to identify and quantify constituents in all waste streams to the extent possible. Second, the emissions were measured under two operating conditions, steady state and with a transient combustion upset. The steady state operation was similar to conditions during a trial burn and the transient upsets were intended to simulate conditions that may occur at times during normal operation.

The test site for this study was selected after a number of sites had been surveyed. It was desirable to select a site that would be most representative of hazardous waste incinerators in the United States. Though it is impossible to be completely representative at any one site, the Dow Chemical Company incinerator in Plaquemine, Louisiana, was chosen because it had many of the equipment components common to hazardous waste incinerators and burned a wide variety of types of wastes. The incinerator consisted of a rotary kiln with liquid waste injection and drummed solid feed, secondary combustion chamber, quench, and particulate and HCl control devices. The wastes fed to the incinerator during the tests included solids and liquids as follows:

- Solids - Substituted cellulose
  - Polyethylene wax
  - Chlorinated pyridine tar
- Organic liquids - Isopar (2,2,4-trimethylpentane)
  - Carbon tetrachloride
- Aqueous liquids - Runoff from diked area

Each type of solid waste was drummed separately and the drums were automatically weighed and fed through a ram feeder to the kiln every 4 minutes (min). Drums of the different types of waste were fed alternately. A uniform supply of the liquid organic waste sufficient for about 100 hours (hr) of operation was accumulated in a tank and spiked with about 10 percent carbon tetrachloride before the test. Liquid organic waste was fed continuously to both the kiln and secondary chamber, and the aqueous liquid waste was fed only to the kiln. Natural gas was fired in both the kiln and secondary chamber as needed to maintain temperatures. Combustion parameters (temperature, airflows, etc.) and all feedrates are controlled by computer from a central control room.

Essentially all input and effluent streams were sampled and analyzed using a wide variety of techniques. Table 1 shows a summary of the sampling and analysis parameters and methods used. EPA's mobile monitoring van assisted MRI with the sampling and Dow Chemical conducted parallel sampling and analysis for many of the measurements (VOST, waste feed, scrubber water outlet).

A sufficient number of the solid waste drums were set aside, numbered, and sampled during the week prior to the test. An equal number of drums containing substituted celloluse, polyethylene wax, and chlorinated pyridine tars were used. The solid waste samples were analyzed for volatile and semivolatile POHCs, chlorides, ash, and heating value. Samples of the liquid organic wastes were taken from a tap at 15-min intervals, as were the aqueous wastes. Both these sample types were analyzed for volatile and semivolatile POHCs, chlorides, ash, and heating value. Viscosity of the liquid organic waste was also measured. The scrubber waters were sampled from a tap at approximately 30-min intervals, and analyzed for POHCs and other major constituents. The bottom ash hopper was emptied at the start of each run and a sample was collected after each test run. The ash samples were analyzed for semivolatile compounds.

The stack sampling included two Modified Method 5 (MM5) trains, a Volatile Organic Sampling train, a midget impinger train for aldehydes, an ORSAT sampler, continuous gas analyzers and three GCs. One MM5 train was analyzed for particulates and anions and the other was analyzed for semivolatile organics. The VOST samples were analyzed for volatile organic constituents. The ORSAT sample was analyzed for O_2 and CO_2. The continuous analyzers included O_2, CO, CO_2, NO_x and THC. The grab sampling frequency for the GCs depended on the column being used and the actual run conditions. The C_1 and C_3 hydrocarbons were detected and quantified using a Porapak QS column and FID. The aromatic compounds were detected and quantified using a Megabore 624 column and a photoionization detector (PID). The halogenated compounds were detected and quantified using a Carbopack 624 column and a Hall detector. The GC techniques used were designed for research measurements and provided intermittent, instantaneous values at selected times.

DISCUSSION OF RESULTS

Process Data and Waste Characteristics

Key process data for each run are presented in Table 2. The process data shown consists of kiln and secondary combustion chamber temperatures, percent O_2, stack flow rate, natural gas heat input, and total heat input. The total heat input is the sum of heat input from the natural gas and waste feed. Ranges for selected process data are shown in parentheses.

Runs 1 through 3 were conducted under steady state operating conditions. However, runs 4 through 6 were altered so that the incinerator operated with a transient combustion upset. Several techniques were attempted to accomplish this transient condition by causing a sudden increase in the feed of volatile waste to the incinerator. Attempts with waste fed to the rotary kiln, spiking 10 gallons (gal.) of volatile hydrocarbons in drums of solid waste or suddenly increasing the liquid waste feed, failed to produce a transient condition. The CO level did not change. A sudden increase in liquid organic waste feed to the secondary chamber did produce sharp increases in CO and THC levels, and that technique was chosen to cause the transient condition.

The liquid organic waste feedrate to the secondary combustion chamber was suddenly increased from a normal 2 gallons per minute (gal/min) to 6 gal/min for approximately 7 seconds (sec) and then returned to the original setting. This fluctuation in the liquid organic waste feedrate occurred 15 min into the run and approximately every 30 min throughout the run. A review of the data in Table 2 shows that the transient conditions did not cause any major change in the process parameters shown on the table.

Table 3 presents the average waste characteristics for the steady state and transient test runs. The characteristics compared are feedrates, heating values, percent chlorine, and percent ash. The waste characteristics did not change significantly between the two sets of test runs.

Carbon Monoxide (CO) and Total Hydrocarbon (THC) Emissions

One way to characterize the operation of the incinerator under steady state and transient conditions is to compare CO and THC levels. Table 4 presents average CO levels and ranges of CO for each run. CO levels for the steady state conditions (runs 1 through 3) averaged near zero while the average for the transient conditions (runs 4 through 6) ranged from 10 to 15 parts per million (ppm). During transient conditions, a CO spike was registered approximately every 30 min with the levels increasing rapidly to about 700 ppm (1-min average) then decreasing quickly.

Table 4 also contains the average and range of THC values for each run. The THC values are calculated as ppm of methane. MRI's runs 1 through 3 showed a steady THC level with averages of 6 to 8 ppm. Dow's average THC level for runs 1 through 3 was less than the detection limit (1 ppm). MRI run 4 had a slightly elevated THC level of 9 ppm and peaks to 160 ppm during the transient upset. MRI runs 5 and 6 had significantly higher THC levels. Run 5 produced an average THC of 150 ppm with peaks up to 220 ppm, while run 6 produced an average of 110 ppm and peaks to 190 ppm. Dow's THC analyzer malfunctioned during run 4. Dow's run 5 produced an average THC of 99 ppm with peaks up to 150 ppm. Run 6 showed an average THC of 60 ppm with peaks up to 63 ppm. These high THC levels were largely accounted for by methane. The difference between run 4 and runs 5 and 6 is under investigation.

Volatile Compound Emissions

Tables 5 and 6 present the stack concentrations of the volatile organic compounds found during the steady state and transient operating conditions, respectively. Results from both MRI sampling and parallel sampling by Dow Chemical are shown. MRI data for run 2 were not available for presentation in this paper. Comparison of the two sets of data provides some perspective on the variability encountered in measurement of these low levels of volatile organic compounds in incinerator stacks. Table 7 shows the average results for the two operating conditions and also presents blank values for MRI's data. The sample values in these tables are not blank corrected; therefore, the values should be viewed relative to the blank values. The acetone values, for example, are uncertain when the blank values are considered. Also, the chloromethane data were obtained from GC analysis of periodic grab samples and may represent a somewhat different average than the other compounds collected in the VOST. Chloromethane has a low boiling point and is not retained well on the Tenax used in the VOST. There were indications in the data that some portion of the chloromethane may also be attributable to blank background levels.

During steady state conditions in runs 1 and 3, methane, chloromethane, and chloroform were emitted at the greatest rates, based on the MRI data. Methane accounted for 27 percent of the total volatile emissions and chloromethane and chloroform accounted for another 7 percent. All other compounds were emitted at much lower levels.

The largest change in concentrations between the steady state conditions and the transient conditions during runs 4 through 6 was a substantial increase in methane emissions. Dichloromethane and benzene also increased significantly, by factors of 30 and 12, respectively. The higher values for these two compounds, however, were still below 100 ppb. No other volatile compounds showed the large increase in concentration as those three compounds. Runs 5 and 6 showed much higher concentrations of methane and dichloromethane than run 4 (see Table 6). This is not explained at this time but is similar to the trend in THC discussed earlier.

To compare the volatile compound emissions to the total THC emissions, all results were converted to an equivalent concentration in parts per billion (ppb) as methane. The conversion factors from ppb to ppb as methane are based on the effective carbon number commonly used in estimating FID response factors and on measured literature values. Table 8 presents a summary of the volatile compound concentrations in ppb as methane. This comparison is useful to assess the degree that total emissions have been identified, but it does distort the relative mass emissions between compounds. Nonchlorinated compounds have a higher response on a FID detector than chlorinated compounds. For example, compare the relative levels of chloroform and benzene on Table 7 versus Table 8.

Table 9 compares the total hydrocarbon concentrations with methane, total volatile and other compounds, based on the data in Table 8. Further analyses are being completed to identify some of the other category. A comparison of the average concentrations of the two sets of runs shows a significant increase in the total hydrocarbon (THC) concentration. Methane concentration increases and also becomes a much larger proportion of the emissions during the transient runs. The volatile compounds increase slightly in concentration but their percent contribution to the total hydrocarbon emissions decreases.

In addition to measurement of emission levels of volatile compounds, the destruction and removal efficiency (DRE) was measured for carbon tetrachloride, the principal volatile compound in the waste. The DREs calculated from the MRI data for the steady state test runs ranged from 99.998 to 99.9995. DREs during the transient test runs were slightly lower, ranging from 99.994 to 99.998. The DREs calculated from the Dow data ranged from 99.9992 to 99.9998 for the steady state runs and from 99.9995 to 99.9997 for the transient runs.

Particulate Matter and HCl Emissions

Table 10 presents the particulate and HCl emissions, and HCl efficiency for each run. The range of particulate emissions was 9.0 to 35 milligrams/cubic meter (mg/m^3). Ash loading to the incinerator was very low compared to typical operation of this incinerator and to typical operation of other rotary kilns that burn hazardous waste. The range of HCl emissions was 0.066 to 0.11 kg/hr. HCl efficiencies averaged 99.95 percent. These rates are all very low compared to the regulatory limits and to typical results from hazardous waste incinerator tests.

CONCLUSIONS

Final conclusions for this project will not be available until all of the data have been analyzed. However, some preliminary conclusions can be reached, based on the data presented in this paper. These conclusions are:

- Methane was a substantial portion of the total hydrocarbons emitted from the hazardous waste incinerator tested. The percent contribution from methane was higher for the transient upset conditions than during steady state operation.
- MRI's preliminary data show a large portion of the total hydrocarbons emitted during steady state operation was not accounted for with the volatile organic compounds identified. Further analysis for semivolatile compounds is expected to account for some of the unidentified portion.
- The change in concentration of volatile compounds between the steady state and transient upset conditions was not uniform across compounds. It appeared to be compound specific.

TABLE 1. SUMMARY OF SAMPLING AND ANALYSIS PARAMETERS AND METHODS

Sample	Sampling method	Sampling frequency for each run	Analytical parameters	Analytical method
Liquid organic waste	Tap (S004)	One grab sample every 15 min composited into one sample for each run	SV organics	GC,MS
			Chlorides	Organic halide (D4327-84 or D808-81)
			Heating value	Calorimeter (D240-73)
			Ash	Ignition (D482-80)
			Viscosity	Viscometer (D-88-81)
	VOA vial[1] filled from composite	One at end of run	V organics[3]	GC/MS
Aqueous waste	Tap (3004)	One grab sample every 15 min composited into one sample for each run	SV organics	GC/MS
			Chlorides	Organic halide (D4327-84 or D808-81)
			Heating value	Calorimeter (D240-73)
			Ash	Ignition (D482-80)
	Tap (S004)	One VOA vial every 15 min	V organics	GC/MS
Solid waste	Scoop (S007)	One grab sample per solid charge, composited at end or test	V organics	GC/MS
			SV organics	GC/MS
			Chlorides	Organic halide (D432-84)
			Heating value	Calorimeter (D2015-77)
			Ash	Ignition (D482-80)
Scrubber feed and effluent water	Dipper (S002)	One grab sample every 30 min composited into one sample each run	SV organics	GC/MS
	VOA vial filled from grab sample	One VOA vial every 30 min	V organics	GC/MS
Ash	Scoop (S007)	One grab sample per run	SV organics	GC/MS
Stack gas	MM5[2]	2-hr composite per run	Particulate	Gravimetric (EPA RM5)
			HCl	Organic halide (D4327-84)
			Moisture	Gravimetric
			Temperature	Thermocouple
			Velocity	Pitot tube

TABLE 1 (Continued)

Sample	Sampling method	Sampling frequency for each run	Analytical parameters	Analytical method
	MM5	2-hr composite per run	SV organics	GC/MS
			Moisture	Gravimetric
			Temperature	Thermocouple
			Velocity	Pitot tube
	VOST (S012)[4]	Three traps pairs at 40 min per pair per run	Method 624 Compounds	GC/MS
	EPA Reference Method 3	One composite sample per run	Oxygen, carbon dioxide	Orsat
	A132	One composite sample per run	Aldehydes	HPLC
	Continuous	1 min averages	CO, CO_2, O_2 NO_x, THC	NDIR, NDIR, paramagnetic, chemiluminescent, FID
	Gas sampling valve	~ once/30 min	C_1 to C_3 hydrocarbons	GC/FID
	Gas sampling valve	~ once/30 min[5]	Aromatics	GC/PID
	Gas sampling valve or syringe	~ once/30 min[5]	Halogenated organics	GC/Hall or PID

NOTE: Sampling method numbers (e.g., S004) refer to methods published in "Sampling and Analysis Methods for Hazardous Waste Combustion," December 1983; analytical methods beginning with prefix D refer to ASTM methods.

[1] Volatile organic analysis vial.

[2] MM5 = Modified Method 5.

[3] Volatile organic constituents.

[4] VOST = Volatile organic sampling train.

[5] Maximum rate permitted by analysis time.

TABLE 2. PROCESS DATA

	Steady state			Transient		
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Kiln temperature (°F)	1550 (1402-1668)	1396 (1317-1547)	1438 (1359-1534)	1439 (1379-1493)	1364 (1255-1559)	1467 (1400-1550)
Secondary combustion temperature (°F)	1858 (1824-1898)	1742 (1714-1806)	1708 (1681-1739)	1800 (1751-1894)	1795 (1753-1832)	1854 (1786-1900)
O_2 (%)	10.1 (9.0-11.3)	11.0 (9.3-11.6)	11.5 (10.2-12.2)	11.2 (10.3-12.1)	10.6 (8.8-11.5)	9.9 (7.9-11.3)
Stack flow rate (acfm)	22,200	21,300	21,300	23,300	25,200	25,100
Natural gas[1] (x 10^6 Btu/hr)	9.0	10	10.2	13.3	14.8	12.8
Total heat input[2] (x 10^6 Btu/hr)	52.9	53.9	49.3	51.5	53.8	58.0

[1] Natural gas heating value of 24,100 Btu/lb was estimated.

[2] Total heat input includes heat input from natural gas.

TABLE 3. AVERAGE WASTE CHARACTERISTICS

	Feedrates (lb/hr) steady state/ transient	HHV (Btu/lb) steady state/ transient	Cl (%) steady state/ transient	Ash (%) steady state/ transient
Solid				
Chlorinated pyridine	1,300/1,350	1,970/1,700	26.40/20.80	35.10/37.60
Polyethylene wax	510/470	15,240/17,100	0.016/0.010	0.16/0.087
Substituted cellulose	1,110/1,230	6,980/6,250	0.39/0.61	4.10/3.00
Liquid organic				
To kiln	520/490	18,000/17,980	10.70/10.80	0.033/0.026
To SCC	820/820	18,000/17,980	10.70/10.80	0.033/0.026
Liquid aqueous	5,010/4,940	15/0	0.0044/0.0023	0.031/0.034

TABLE 4. PRELIMINARY AVERAGE CO AND THC LEVELS

Run	CO (ppm)		THC (ppm)	
	EPA van	Dow	MRI	Dow
1	~ 1	3.5	7.6	0
	(0-86)	(3-4)	(7.4-9.0)	
2	NA	3.5	6.8	0
		(2.6-4.7)	(5.8-7.9)	
3	~ 1	2.7	6.2	0
	(0-2.6)	(2.5-3.3)	(4.9-10.0)	
4	10	20	8.8	NA
	(0-720)	(2-691)	(4.1-160)	
5	11	7.9	150	99
	(0.58-710)	(1.6-538)	(100-220)	(79-150)
6	15	33	110	60
	(0.03-710)	(6.2-819)	(79-190)	(55-63)

TABLE 5. PRELIMINARY STACK CONCENTRATIONS OF VOLATILE COMPOUNDS FOR STEADY-STATE RUNS (ppb) (NOT BLANK CORRECTED)

Compound	MRI run 1	Dow run 1	Dow run 2	MRI run 3	Dow run 3
Methane	1,700[1]	NA[4]	NA	1,300[1]	NA
Chloromethane	220[1]	30	3.7	100[1]	ND[2]
Dimethyl ether	19	NQ[3]	NQ	0.63	NQ
Methyl bromide	0.051	ND	ND	0.15	ND
Vinyl chloride	0.86	2.1	ND	1.2	ND
Methylene chloride	3.7	0.85	0.68	1.7	0.77
Acetone	8.7	NQ	NQ	7.9	NQ
Trichlorofluoromethane	4.2	NQ	NQ	0.18	NQ
1,1-Dichloroethylene	0.99	ND	0.020	0.050	0.017
Chloroform	63	16	31	65	26
1,2-Dichloroethane	2.7	1.2	1.3	0.22	0.16
1,1,1-Trichloroethane	0.25	0.16	1.5	1.2	0.83
Carbon tetrachloride	3.9	2.0	0.83	1.3	0.61
Dichlorobromomethane	14	4.4	5.6	13	5.7
Benzene	4.9	8.0	11	2.1	3.4
Chlorodibromomethane	2.3	1.3	0.91	1.7	0.80
2-Chloroethyl vinyl ether	2.0	ND	ND	0.25	ND
Bromoform	0.14	1.2	0.083	0.029	0.044
1,1,2,2-Tetrachloroethylene	1.2	0.36	0.33	0.41	0.30
C_8H_{18}	1.2	ND	ND	0.76	ND
Toluene	7.9	7.3	2.4	0.94	4.7
Chlorobenzene	0.11	0.060	0.12	0.086	0.086
Ethylbenzene	1.0	0.66	0.22	0.14	0.061
Total	2,100	NA	NA	1,500	NA

[1] Data from GC analysis of grab samples; other data from GC/MS analysis of VOST samples.

[2] ND = Not detected.

[3] NQ = Not quantitated. Compound detection was qualitative by GC/MS. Quantitation will be made available for final report.

[4] NA = Not available.

TABLE 6. PRELIMINARY STACK CONCENTRATIONS OF VOLATILE COMPOUNDS FOR TRANSIENT RUNS (ppb) (NOT BLANK CORRECTED)

Compound	MRI run 4	Dow run 4	MRI run 5	Dow run 5	MRI run 6	Dow run 6
Methane	4,400[1]	NA[4]	93,000[1]	NA	51,000[1]	NA
Chloromethane	200	2.3	200[1]	140	310[1]	81
Dimethyl ether	1.4	NQ[2]	1.5	NQ	1.5	NQ
Methyl bromide	2.3	ND[3]	3.8	ND	4.3	3.0
Vinyl chloride	0.74	ND	1.8	ND	2.8	0.70
Methylene chloride	5.4	1.7	150	40	91	37
Acetone	13	NQ	12	NQ	12	NQ
Trichlorofluoromethane	0.26	NQ	0.39	NQ	0.75	NQ
1,1-Dichloroethylene	0.12	ND	0.27	0.070	0.25	0.12
Chloroform	73	28	24	3.8	18	9.9
1,2-Dichloroethane	0.54	0.49	0.097	0.056	0.46	0.34
1,1,1-Trichloroethane	0.74	0.40	0.40	0.20	0.22	0.25
Carbon tetrachloride	7.4	0.69	11	1.1	3.3	1.1
Dichlorobromomethane	16	6.8	1.2	0.18	2.9	2.1
Benzene	62	25	19	11	56	7.4
Chlorodibromomethane	4.6	0.52	0.54	0.15	0.35	0.16
2-Chloroethyl vinyl ether	1.4	ND	2.2	ND	0.66	ND
Bromoform	6.4	11	0.64	0.47	0.11	0.12
1,1,2,2-Tetrachloroethylene	0.25	0.16	0.16	0.039	0.087	0.0087
C_8H_{18}	44	NQ	3.6	NQ	< 0.0085	NQ
Toluene	1.7	1.4	0.92	11	0.71	2.0
Chlorobenzene	0.56	0.19	0.58	0.36	0.60	0.54
Ethylbenzene	0.80	0.041	0.18	0.034	0.11	0.045
Total	4,800	NA	94,000	NA	52,000	NA

[1] Data from GC analysis of grab samples; other data from GC/MS analysis of VOST samples.

[2] NQ = Not quantitated. Compound detection was qualitative by GC/MS. Quantitation will be made available for final report.

[3] ND = Not detected.

[4] NA = Not available.

TABLE 7. PRELIMINARY AVERAGE STACK CONCENTRATIONS AND BLANK VALUES OF VOLATILE COMPOUNDS (ppb) (NOT BLANK CORRECTED)

Compound	Steady-state		Transient		MRI VOST blanks	
	Average MRI runs 1&3	Average Dow runs 1-3	Average MRI runs 4-6	Average Dow runs 4-6	Average	Range
Methane	1,500[1]	NA[2]	49,000	NA	NA	NA
Chloromethane	160[1]	NQ[3]	240	76	NA	NA
Dimethyl ether	10	NA	1.4	NA	1.2	ND-1.2
Methyl bromide	0.10	NA	3.5	NA	ND[4]	ND
Vinyl chloride	1.0	NA	1.8	NA	1.2	ND-1.2
Methylene chloride	2.7	0.77	82	26	3.8	0.35-12
Acetone	8.3	NA	12	NA	7.6	0.64-31
Trichlorofluoromethane	2.2	NA	0.47	NA	0.19	0.0016-0.81
1,1-Dichloroethylene	0.52	NA	0.22	NA	ND	ND
Chloroform	64	24	38	14	0.13	ND-0.25
1,2-Dichloroethane	1.4	0.90	0.37	0.29	0.049	0.0036-0.15
1,1,1-Trichloroethane	0.70	0.84	0.45	0.28	0.022	ND-0.030
Carbon tetrachloride	2.6	1.2	7.4	0.98	0.35	ND-0.35
Dichlorobromomethane	14	5.2	6.8	3.0	ND	ND
Benzene	3.5	7.6	46	14	1.0	0.40-2.2
Chlorodibromomethane	2.0	0.99	1.8	0.28	ND	ND
2-Chloroethyl vinyl ether	1.1	NA	1.4	NA	0.31	ND-0.41
Bromoform	0.086	0.46	2.4	4.0	0.0054	ND-0.0054
1,1,2,2-Tetrachloroethylene	0.81	0.33	0.17	0.069	0.026	ND-0.073
C_8H_{18}	0.99	NA	16	NA	0.58	ND-0.58
Toluene	4.4	4.8	1.1	4.9	0.32	ND-1.5
Chlorobenzene	0.096	0.088	0.58	0.36	0.025	ND-0.052
Ethylbenzene	0.58	0.31	0.36	0.040	0.035	ND-0.091
Total	1,800	NA	49,000	NA		

[1] Data from GC analysis of grab samples; other data from GC/MS analysis of VOST samples.

[2] NA = Not available.

[3] NQ = Not quantitated. Compound detection was qualitative by GC/MS. Quantitation will be made available for final report.

[4] ND = Not detected.

TABLE 8. PRELIMINARY STACK CONCENTRATIONS OF VOLATILE COMPOUNDS CALCULATED AS EQUIVALENT THC, ppb METHANE

Compound	Run 1	Run 3	Average runs 1&3	Run 4	Run 5	Run 6	Average runs 4-6
Chloromethane	21	98	150	190	190	300	230
Dimethyl ether	29	1.0	15	2.1	2.2	2.2	2.2
Methyl bromide	< 0.04	0.1	0.1	2.2	3.6	4.0	3.3
Vinyl chloride	1.5	2.1	1.8	1.2	3.1	4.9	3.1
Dichloromethane	3.3	1.5	2.4	4.9	140	82	75
Acetone	18	15	17	26	24	25	25
Trichlorofluoromethane	1.9	0.1	1.0	0.1	0.2	0.3	0.2
1,1-Dichloroethylene	1.6	0.1	0.9	0.2	0.4	0.4	0.3
Chloroform	53	55	54	61	21	15	32
1,2-Dichloroethane	4.1	0.3	2.2	0.9	0.2	0.8	0.6
1,1,1-Trichloroethane	0.4	1.8	1.1	1.1	0.6	0.3	0.7
Carbon tetrachloride	2.5	0.8	1.7	4.7	7.3	2.1	4.7
Dichlorobromomethane	12	11	12	14	1.0	2.5	5.8
Benzene	30	13	22	370	120	330	270
Chlorodibromomethane	1.9	1.5	1.7	4.0	0.5	0.3	1.6
2-Chloroethyl vinyl ether	6.3	0.8	3.6	4.4	7.2	2.1	4.5
Bromoform	0.1	< 0.04	0.1	5.4	0.5	0.1	2.0
1,1,2,2-Tetrachloroethylene	1.3	0.4	0.9	0.3	0.2	0.1	0.2
C8H18	9.9	6.2	8.1	350	29	< 0.04	126
Toluene	56	6.5	31	12	6.4	5.1	7.7
Chlorobenzene	0.7	0.5	0.6	3.4	3.4	3.5	3.4
Ethylbenzene	8.2	1.1	4.7	6.3	1.5	0.9	2.9
Total	460	220	340	1,100	550	780	800

TABLE 9. PRELIMINARY MRI CONCENTRATIONS AS A PERCENT OF TOTAL HYDROCARBONS

	THC (ppm)*	Methane		Total volatiles		Other
		(ppm)*	% Total	(ppm)*	% Total	% Total
Run 1	7.6	1.7	22	0.58	8	70
Run 3	6.2	1.3	21	0.23	4	75
Run 4	8.8	4.3	49	1.1	13	38
Run 5	145	93	64	0.58	0.4	36
Run 6	106	51	48	0.84	0.8	51
Averages:						
Runs 1&3	6.9	1.5	22	0.41	6	72
Runs 4-6	87	49	56	0.85	1	43

* All ppm units are as methane.

TABLE 10. PRELIMINARY PARTICULATE AND HCl EMISSIONS

Run	Particulate (mg/m³)	HCl emissions[1] (kg/hr)	HCl efficiency[1]
1	15.9	0.066	0.99981
2	14.2	0.074	0.99948
3	9.0	0.074	0.99956
4	11.1	0.11	0.99918
5	23.6	0.081	0.99963
6	35.5	0.11	0.99955

[1] Average of two values.

INCINERATION OF CLEANUP RESIDUES FROM THE BRIDGEPORT RENTAL AND OIL SERVICES SUPERFUND SITE

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ABSTRACT

Several PCB-contaminated wastes will be generated through remedial actions at the Bridgeport Rental and Oil Services (BROS) Superfund site in Bridgeport, New Jersey. Among these are a lagoon surface oil, an underlying sludge, and contaminated soil. Incinerability testing of these three wastes plus a combination of the soil and sludge was performed at the Environmental Protection Agency's (EPA) Combustion Research Facility (CRF) to determine whether thermal treatment via incineration was a viable treatment option for these wastes. Tests under three incinerator operating conditions were performed in the CRF rotary kiln incineration system for each waste. Test variables included rotary kiln temperature and rotation speed (solids residence time) and afterburner temperature. All wastes contained between 100 and 300 ppm polychlorinated biphenyls (PCBs) as Arochlor 1254. PCB destruction efficiency (DE) was in the 99.99 to 99.999 percent range for all tests. All scrubber blowdown samples had nondetectable PCB levels (<1 ppb) and hazardous constituent trace element concentrations well below extraction procedure (EP) toxicity thresholds. Kiln ash samples for the soil, sludge, and soil/sludge wastes were not PCB contaminated, having nondetectable PCB levels (<0.4 ppm). The composite kiln ash for the lagoon surface oil tests contained 2.6 ppm PCB. EP leachates of all kiln ash samples had hazardous constituent trace element concentrations well below EP toxicity thresholds.

INTRODUCTION

One of the primary functions of the Combustion Research Facility (CRF) is to support the Environmental Protection Agency (EPA) Regional Offices in evaluations of incineration as a disposal option for wastes generated through remedial actions taken at Superfund sites. This report summarizes test results obtained during the incineration of hazardous wastes from the Bridgeport Rental and Oil Services (BROS) Superfund site located in Bridgeport, New Jersey. Several PCB-contaminated wastes that will be generated from the BROS site are being considered for thermal treatment using incineration. Among these wastes are PCB-contaminated lagoon surface oil, lagoon sludge, and contaminated soil. The primary objective of the CRF tests was to determine whether these PCB-contaminated wastes could be treated via conventional incineration to render them uncontaminated, while meeting a PCB destruction efficiency (DE) of 99.9999 percent, as mandated under the Toxics Substances Control Act (TSCA). Emissions of products of incomplete combustion (PICs) in the flue gas and the EP toxicity trace element content of incinerator residual streams were also investigated.

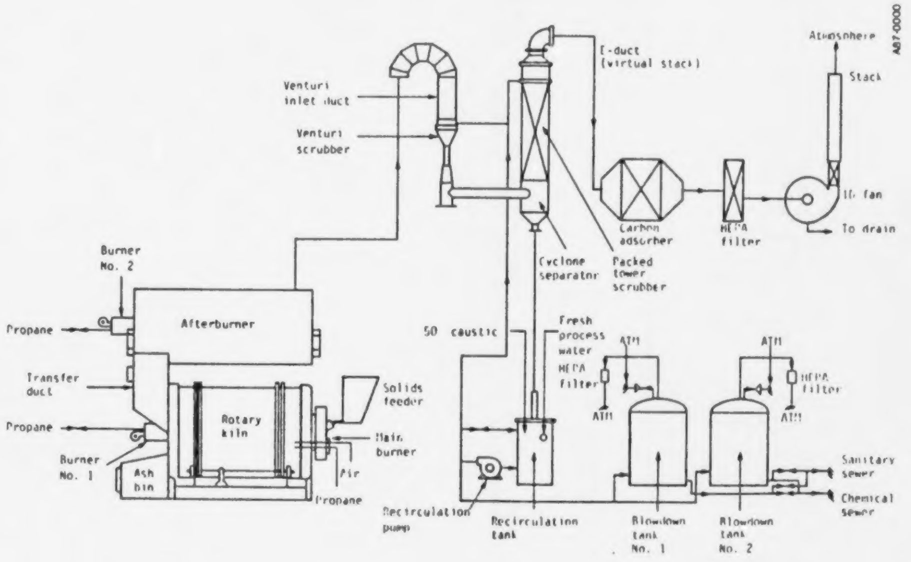
APPROACH

The CRF rotary kiln system, depicted in Figure 1, was used to incinerate the wastes during these tests. The primary rotary kiln chamber has a maximum design temperature of about 900°C (1,650°F) with a nominal bulk gas residence time of about 1.7 sec. Further thermal treatment takes place in the afterburner chamber which is designed for a maximum temperature of approximately 1,200°C (2,200°F) and a bulk residence time of about 1.0 sec at a typical excess oxygen level of 8 percent. The air pollution control system consists of a venturi and a packed column scrubber, followed by a carbon adsorber and a high efficiency particulate filter.

Four waste materials were tested during this program. The chemical composition and PCB and metals concentrations of each waste material are summarized in Table 1. The lagoon surface oil, a dark brown viscous fluid containing some debris, was pumped in the kiln via a progressive cavity pump. The sludge, a black aqueous gel also containing much debris, was also fed into the kiln via the progressive cavity pump. The contaminated soil, a clumped clay mud containing the most debris (rocks, grass, roots, twigs) was fed into the kiln using 5.7L (1.5 gal) fiberpacks via the available ram feeder. The mixture of sludge and soil was also fed in fiberpacks via the ram feed system.

PCB contamination in these test waste materials ranged from about 100 mg/kg for the soil and soil/sludge mixture to nearly 300 mg/kg for the lagoon surface oil. Highest concentrations of hazardous constituent trace metals were measured for lead (46 to 2,900 mg/kg). Barium and chromium were also detected in each test material in the range of 12 to 1,030 mg/kg. Leachate analyses of each test material showed trace elements concentrations well below the EP toxicity limits. Thus, these test materials would not be considered hazardous wastes under RCRA but, because of PCB contamination, they are considered hazardous under TSCA provisions.

Table 2 summarizes the average incinerator conditions during each test. A


A87-0000
Atmosphere
Stack
E-duct
(virtual stack)
Venturi
inlet duct
Venturi
scrubber
ID fan
To drain
Carbon
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HEPA
filter
Cyclone
separator
Packed
tower
scrubber
Burner
No. 2
Propane
Afterburner
50 caustic
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process
water
HEPA
filter
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Transfer
duct
Solids
feeder
Rotary
kiln
Propane
Main
burner
Burner
No. 1
Ash
bin
Air
Propane
Sanitary
sewer
Chemical
sewer
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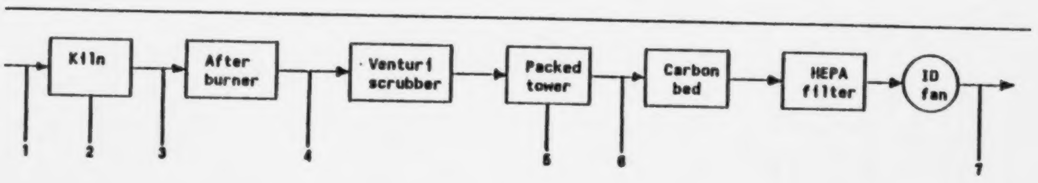
Blowdown
tank
No. 1
Blowdown
tank
No. 2

Figure 1. Rotary kiln incinerator system.


Kiln
After burner
Venturi scrubber
Packed tower
Carbon bed
HEPA filter
ID fan
1
2
3
4
5
6
7

	Parameter										
Sampling point	Waste feedrate	Waste feed	Fuel feedrate	Air feedrate	Kiln ash	Scrubber blowdown	CM's (O_2, CO_2)	Volume flow	MM5 (particulate, PCBs, and semivolatile organics)	VOST (volatile organics)	Method 5 (Particulate)
1	X	X	X	X							
2					X						
3							X				
4							X				
5						X		X			X
6							X	X	X	X	
7							X	X			X

T: Temperature
P: Pressure
RH: Relative Humidity

Figure 2. Sampling protocol.

TABLE 1. BROS WASTE CHARACTERIZATION -- COMPOSITION

Ultimate analysis (% by weight as fed)	Area 1 soil	Lagoon surface oil	Lagoon sludge	Soil and lagoon sludge
C	11.4	54.4	1.0	13.1
H	4.6	10.9	11.1	4.7
O	25.0	29.9	81.8	32.2
N	0.1	0.1	1.0	0.4
S	0.4	0.7	1.0	0.01
Cl	0.44	0.1	0.01	0.06
Total	41.94	96.1	95.91	50.86
High heating value, MJ/kg (Btu/lb)	0	8.62 (3,716)	10.0 (4,348)	2.43 (1,048)
Total PCBs (mg/kg as Arochlor 1254)	67.3-167 (110)[a]	270-300 (286)[b]	250	78.6-170 (123)[b]
Metals (mg/kg):				
Arsenic, As	<1	2	<1	11
Barium, Ba	744	1,035	23	823
Cadmium, Cd	<1	<10	<5	4
Chromium, Cr	55	46	12	65
Lead, Pb	756	2,888	46	1,034
Mercury, Hg	<1	<1	<1	<1
Selenium, Se	<1	<1	<1	<1
Silver, Ag	<5	<10	<5	<5
EP toxicity leachate (mg/L):				
Arsenic, As (5.0)	<0.1	<0.1	0.19	0.1
Barium, Ba (100)	0.12	<0.1	<0.1	0.30
Cadmium, Cd (1.0)	<0.1	<0.1	<0.1	<0.1
Chromium, Cr (5.0)	<0.1	<0.1	<0.1	<0.1
Lead, Pb (5.0)	0.46	<0.1	<0,1	0.12
Mercury, Hg (0.2)	<0.1	<0.1	<0.1	<0.1
Selenium, Se (1.0)	<0.1	<0.1	<0.1	<0.1
Silver, Ag (5.0)	<0.1	<0.1	<0.1	<0.1

[a] Average value of 9 analyses on 3 composite samples
[b] Average value of 3 analyses on 1 composite sample

TABLE 2. AVERAGE TEST CONDITIONS

Test	Feed method	Feedrate kg/hr (lb/hr)	Kiln rotation speed (rpm)	Kiln		Afterburner	
				Temperature °C (°F)	Exit O_2 (percent dry)	Temperature °C (°F)	Exit O_2 (percent dry)
Lagoon surface oil							
Test 1	Progressive	18 (39)	0.5	667 (1,250)	12.6	1,140 (2,080)	5.6
Test 2	cavity	20 (45)	0.5	677 (1,250)	10.4	1,210 (2,210)	6.0
Test 3	pump	24 (53)	0.5	893 (1,640)	10.3	1,130 (2,070)	6.5
Soil							
Test 1	Fiberpack	44 (98)	0.2	927 (1,700)	8.2	1,130 (2,060)	8.0
Test 2	drum	44 (96)	0.2	700 (1,290)	10.3	1,130 (2,060)	7.2
Test 3	ram-feed	45 (100)	0.2	888 (1,630)	8.8	1,120 (2,050)	6.7
Soil plus sludge							
Test 1	Fiberpack	42 (92)	0.2	715 (1,320)	13.1	1,120 (2,050)	8.5
Test 2	drum	42 (92)	0.2	800 (1,650)	NA	1,120 (2,050)	7.5
Test 3	ram-feed	43 (95)	0.4	893 (1,640)	9.8	1,120 (2,050)	6.8
Sludge							
Test 1	Progressive	40 (88)	0.4	654 (1,210)	NA	1,120 (2,040)	10.1
Test 2	cavity	35 (78)	0.4	882 (1,620)	NA	1,130 (2,050)	6.2
Test 3	pump	33 (72)	0.4	654 (1,210)	NA	1,210 (2,210)	6.2

total of 12 tests were performed, 3 for each of the waste materials, with variable kiln and afterburner temperatures, excess oxygen levels, and kiln rotational speed. The effect of maximum afterburner temperature in combination with low kiln temperatures was investigated during two tests, one with the lagoon surface oil and the other with the sludge as waste feed materials. All other tests were performed with afterburner temperatures at approximately 1,120°C (2,050°F). Propane was used as the primary fuel in both the kiln and afterburner chambers to maintain test temperatures. An increase in excess oxygen at the afterburner exit from 5 to 10 percent corresponds to an approximate 45 percent increase in gas flowrate at constant temperature. This increase in gas flowrate translates to a corresponding reduction in bulk gas residence time.

Figure 2 illustrates the sampling protocol used during these tests. Organic compound emissions were measured at the packed scrubber outlet location and upstream of the carbon bed absorber, using standard EPA methods (2,4). Particulate mass and HCl emissions were measured at three locations, namely afterburner exit, packed scrubber outlet, and stack, using the EPA Method 5 modified for acid gas (HCl) collection in the impinger section of the sampling train (5). The kiln ash and scrubber blowdown were also sampled for priority pollutant metals and organic contents. Analytical methods conformed to those prescribed in References 1 and 3.

TEST RESULTS

PCB destruction measured during these tests generally ranged between 99.99 and 99.999 percent as illustrated in Figure 3. None of the test conditions investigated resulted in a DE of 99.9999 percent required under TSCA provisions for PCB incineration. Attempts to correlate DE results with individual process parameters did not reveal any statistically significant correlations. However, test data illustrated in Figure 4 may indicate a tentative effect of reduced gas residence time at temperature on measured DE. In this figure, the DE is plotted versus a mean gas temperature, defined by the arithmetic average of kiln and afterburner temperatures, normalized by the gas flowrate through the afterburner. The linear regression line shows a relatively good fit (correlation coefficient = 0.82) with increasing DE as temperature and gas residence time increase. Extrapolation of the linear fit to 99.9999 percent DE would indicate a gas flowrate requirement of about 1.2 m^3/sec for a mean temperature of

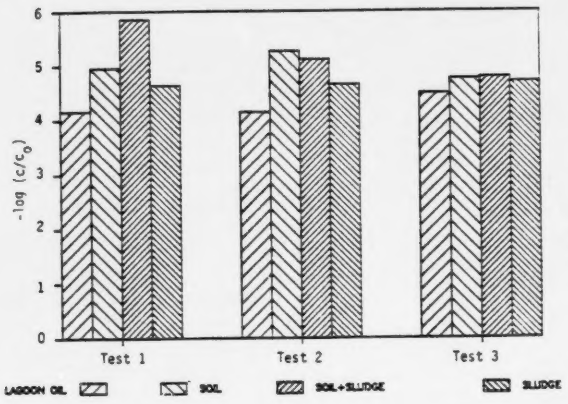


Figure 3. PCB DEs.

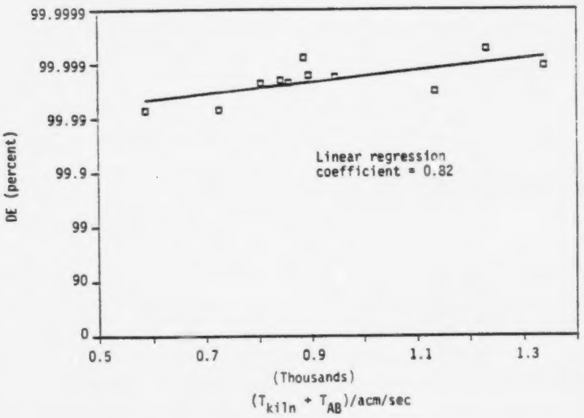


Figure 4. PCB DE vs. temperature/flowrate (°F/acm/sec).

970°C (1,780°F). This gas flowrate corresponds to a residence time in the afterburner of 2.0 sec or about 2.3 times that recorded during these tests.

Table 3 summarizes the concentrations of most common volatile organic compounds detected in the waste feed materials and the incineration effluents. Flue gas concentrations of individual compounds were generally below 10 µg/dscm (approximately 1 ppb). Particulate mass and HCl emissions were measured at levels below those mandated by RCRA regulations (180 mg/dscm corrected to 7 percent O_2 and 1.8 kg/hr, respectively) for all tests as shown in Table 4. Highest particulate levels were recorded during incineration of contaminated soil.

Table 5 summarizes the concentrations of most common trace elements detected in the kiln ash and its leachate and in the scrubber blowdown solids and liquids. The kiln ash was found to contain barium, chromium, and lead in concentrations ranging from about 100 to 2,160 mg/kg. Lead concentrations in the kiln ash and blowdown solids for the soil and soil plus sludge tests clearly reveal partitioning of this metal to the flyash rather than the kiln ash. The partitioning is not evident for the other metals. Kiln leachate analyses and blowdown liquids indicate concentrations typically less than 1 mg/L or well below the EP toxicity levels.

ACKNOWLEDGMENTS

This research was performed under the Combustion Research Facility operations and research contract with the U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory. The invaluable assistance and guidance provided by the EPA Project Officer, Robert Mournighan are gratefully acknowledged. The authors would also like to thank Ronald Borsellins of EPA Region II, and Henry Munoz of the U.S. Army Corps of Engineers for their significant contributions to this effort.

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TABLE 3. MOST COMMON VOLATILE ORGANICS

Compound	Feed concentration (ppm)			Scrubber exit flue gas concentration (μg/dscm)			
	Lagoon surface oil	Sludge	Soil + sludge	Lagoon surface oil	Soil	Sludge	Soil + sludge
1,1-dichloroethylene	4.7	ND	15	ND	ND-2.4	ND	ND
Chloroform	27	ND	ND	ND-5	2.4-2.7	5.8-9.2	3.2-5.3
1,2-dichloroethane	16	14	59	5-31	ND-16	ND	ND
Carbon tetrachloride	68	63	57	6-76	4.4-17	ND-5.1	14-18
1,2-dichloropropane	4	25	ND	ND	ND	0.7-1.4	ND
Trichloroethylene	21	12	5	ND	ND	2.1-3.5	ND
Benzene	3.7	2.1	ND	ND-1,730	0.7-1.4	6.5-8.4	1.2-2.0
Hexane	23	6.0	ND	ND-6	0.6-3	2.2-9.3	1-1-0
Tetrachloroethylene + Tetrachloroethane	ND	16	ND	2-7.5	7.4-17	ND-8.8	2.0-6.6
Toluene	44	4.7	5.1	2-10	7-12	2.9-5.1	3.4-5.2

TABLE 4. SUMMARY OF PARTICULATE AND HCl EMISSIONS

Waste feedstock	Afterburner exit (Location 4)		Scrubber discharge (Location 6)	Stack (Location 7)	
	Particulate mg/dscm[a]	HCl mg/dscm	Particulate mg/dscm[a]	Particulate mg/dscm[a]	HCl mg/dscm
Lagoon surface oil	8.30-17.9 (13.1)[b]	9.60-17.3 (13.2)	<0.2-0.5 (0.33)	NA	NA
Soil	48.8-279 (126)	16.8-30.9 (21.9)	9.70-16.9 (13.1)	13.7-26.1 (19.4)	<9.6
Sludge	18.3-31.9 (27.1)	4.90-7.20 (5.90)	4.70-8.00 (6.60)	12.5-45.7 (23.6)	<9.8
Soil plus sludge	15.8-224[c] (112)	17.8-23.2 (20.6)	9.30-124 (47.6)	39.6-182 (129)	<10.0

[a] Particulate matter concentration corrected to 7 percent plus O_2

[b] Number in parenthesis is the arithmetic average of three tests

[c] Data suspect due to unusually high proportion of particulate catch in the probe rins

NA -- Not available. Samples not taken.

TABLE 5. TRACE ELEMENT CONCENTRATIONS

Test/sample	Arsenic	Barium	Chromium	Lead
Lagoon Surface Oil				
Composite	<2	120	1,090	2,160
Composite kiln ash leachate (mg/L)	0.33	0.33	<0.1	0.23
Average blowdown liquids (mg/L)[a]		0.54	0.16	0.70
Soil				
Average kiln ash (ppm)[a]	<2	550	130	910
Average kiln ash leachate (mg/L)[a]		0.45	<0.1	<0.1
Average blowdown solids (ppm)[b]	<60	980	100	2,400
Average blowdown liquid (mg/L)[a]		0.33	0.29	1.3
Sludge				
Composite kiln ash (ppm)	<2	680	110	800
Composite kiln ash leachate (mg/L)		<0.1	<0.1	0.12
Average blowdown liquid (mg/L)[a]		0.41	0.17	<0.1
Soil plus Sludge				
Average kiln ash (ppm)[a]	<2	740	87	450
Average kiln ash leachate (mg/L)[a]		0.32	<0.1	<0.1
Average blowdown solids (ppm)	<24	820	74	5,010
Average blowdown liquid (mg/L)[a]		0.37	0.31	0.12

[a] Average over three tests.
[b] Average over Tests 2 and 3 only. Test 1 blowdown contained no solids.

Note: EP toxicity limits are 5.0 mg/L for arsenic, chromium and lead, and 100 mg/L for barium.

4. Schlickenreider, Lynn M., Jeffrey W. Adams, and Kathleen E. Thrun, 1975. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003, U.S. EPA, AEERL, Research Triangle Park, North Carolina 27711, February 1985.

5. 40 CFR Part 60, Appendix A.

PILOT-SCALE TESTING OF NONSTEADY BOILER WASTE COFIRING

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ABSTRACT

Waste destruction efficiencies were measured for volatile and semivolatile chlorinated organic compounds cofired with gas, oil, and coal in a pilot-scale boiler simulator with a maximum capacity of 3 million Btu/hr. The tests were run to help interpret waste destruction data from 14 prior boiler cofiring field test programs. Specific issues addressed in the pilot-scale tests were: what is the background level of waste emissions due to residual deposition on boiler surfaces?; what operating conditions fail to yield acceptable destruction efficiency?; what waste products of incomplete combustion are formed, and in what quantities?; and what is the form and fate of trace metals contained in the waste? Operating parameters varied were excess O_2; atomization patterns; residence time; firing rate; wall cooling; and waste or fuel flow transients.

INTRODUCTION

Since 1981, the Environmental Protection Agency (EPA) has tested 14 industrial boilers for performance in the thermal destruction of hazardous wastes cofired with conventional fuels (1). The test facility specifications and operating conditions were selected to obtain a reasonable coverage of the diverse range of industrial boiler designs and operating practices. Field test data were obtained for the following range of conditions:

- Firetube, package and field erected watertube designs; 0.3 to >2 seconds residence time in main firebox
- 2,500 to 350,000 lb/hr steam capacity
- Gas, oil, coal, and wood fuels
- Volatile and semivolatile wastes with heating value from 0 to 18,000 Btu/lb
- 0 to 100 percent heat input from wastes

The results of these 14 tests showed an overall mass weighted waste destruction efficiency of 99.998 percent. This high level of destruction was generally exhibited across the broad range of designs, waste characteristics, and operating conditions tested, and prevailed even when the boilers were intentionally operated in off-design upset conditions such as substoichiometric air, malfunctioning atomizers and waste flow transients. In fact, the destruction efficiencies were uniformly so high that it was not possible within the constraints of plant operation to identify the operational boundary between acceptable and unacceptable destruction efficiencies. This remains an open issue.

Within the context of these high destruction efficiencies, several patterns in the data recurred at most of the sites. Although the average destruction efficiency was nearly five nines, the data did exhibit variability of up to an order of magnitude which was apparently not due to artifacts in the sampling and analysis scheme or to contamination. Additionally, the variations did not correlate with any boiler operational setting or with boiler performance indicators such as CO or NO_x emissions, or smoke. It was also observed at several sites that the stack concentrations of waste species continued for several hours after waste firing was curtailed. This hysteresis effect may be attributable to deposition of trace concentrations of waste species on boiler surfaces, particularly on areas with carbonaceous deposits from oil or coal firing.

Soot blowing, the regular steam cleaning of the boiler heat transfer surfaces, is a normal part of boiler operation. Limited data were obtained during the previous tests indicating that organics were present in higher concentrations during the soot blow cycle. Only the gaseous portion of the flue gas was analyzed due to the characteristics of the sampling systems. Species and concentration of organics adsorbed on the carbonaceous and solid materials being expelled during soot blowing cycles were not determined.

Other significant issues remained at the conclusion of the 14 full-scale boiler tests.

A key issue is the identification of the form and fate of heavy metals. Very little data in this area has been generated by the previous testing for which the emphasis was destruction efficiency (DRE). The effectiveness of air pollution control devices is also not well defined.

A second issue is the more complete identification of products of incomplete combustion (PICs). Several tests showed PIC emissions in boilers as a higher fraction of the organic constituents in the flue gas than those in incinerators. The types and concentrations of PICs resulting from fuels in comparison to cofired waste have not been identified in sufficient detail.

A third issue is the interpretation of data from field tests in the presence of background variability and how this variability relates to the condition of boiler heat exchange surfaces and operating conditions. Some understanding of this issue is needed to gauge the confidence level of conclusions to be reached regarding the relative insensitivity of waste destruction to boiler operating conditions.

The present pilot-scale tests addressed the above issues. The pilot-scale approach was selected over full-scale testing for a number of reasons. The range of parametric variation and degree of off-specification operation envisioned would be difficult to achieve at full-scale field installations. Additionally, the experiments could be more closely controlled at a test facility. There would also be some cost savings realized in conducting pilot-scale testing at a home facility as compared to maintaining a test team at a field facility.

FACILITY

The pilot-scale facility is a refractory-lined furnace and convective section designed with geometric similarity and time-temperature simulation of a tangentially or wall-fired watertube boiler (Figure 1). For the present tests, the unit was fired in the wall-fired mode, typically with gas, oil, or coal fired through three of the burners and a simulated waste through the remaining burner. The fuel feed system, cooling system, and postcombustion cleanup system are shown schematically in Figure 2. For most tests, the unit was fired at a firing rate of 1.5 million Btu/hr which gives a residence time in the firebox prior to quenching in the convective section of approximately 2 seconds. The wall-fired burners were variable swirl research burners equipped with a single fuel injector tube. Combustion air is preheated to 400°F upstream of the burner by an electric heater. For oil firing, steam atomization is typically used, although air atomization is available. The convective section consists of approximately 20 tube

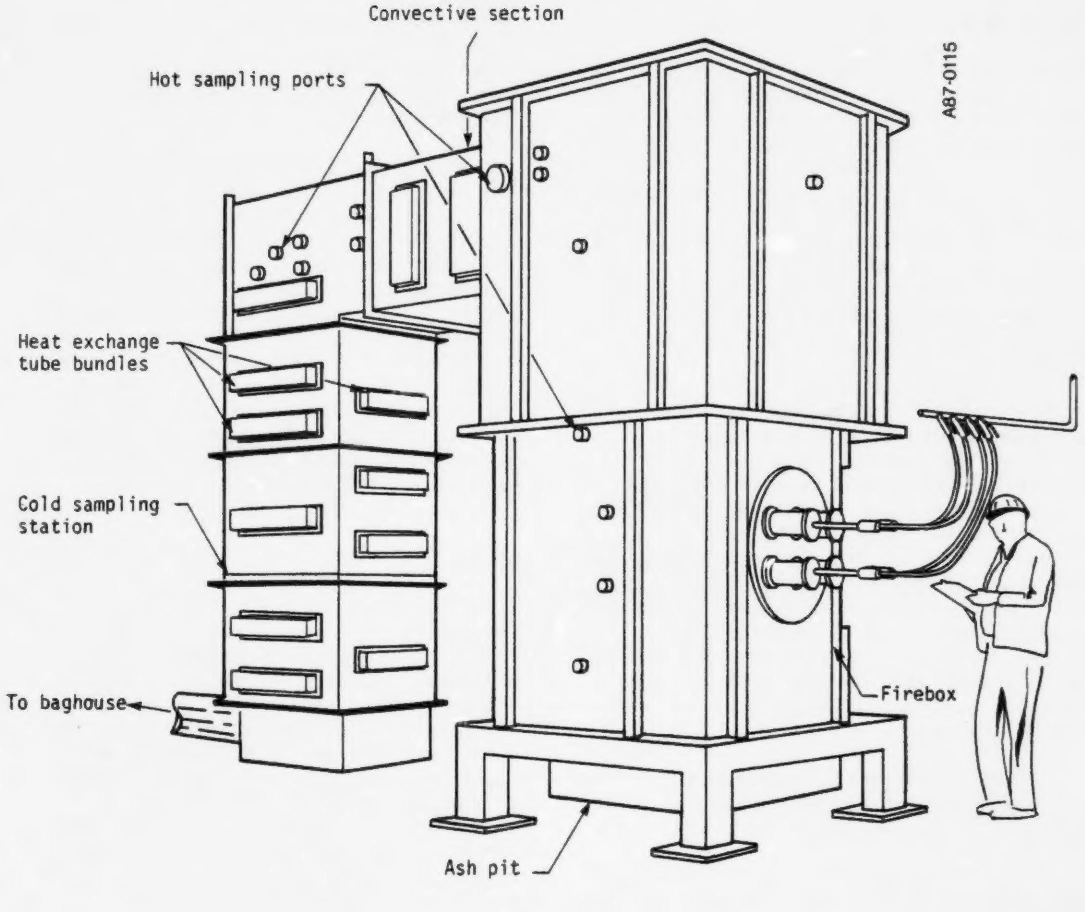
Convective section
Hot sampling ports
A87-0115
Heat exchange tube bundles
Cold sampling station
To baghouse
Firebox
Ash pit

Figure 1. Pilot-Scale Experimental Furnace

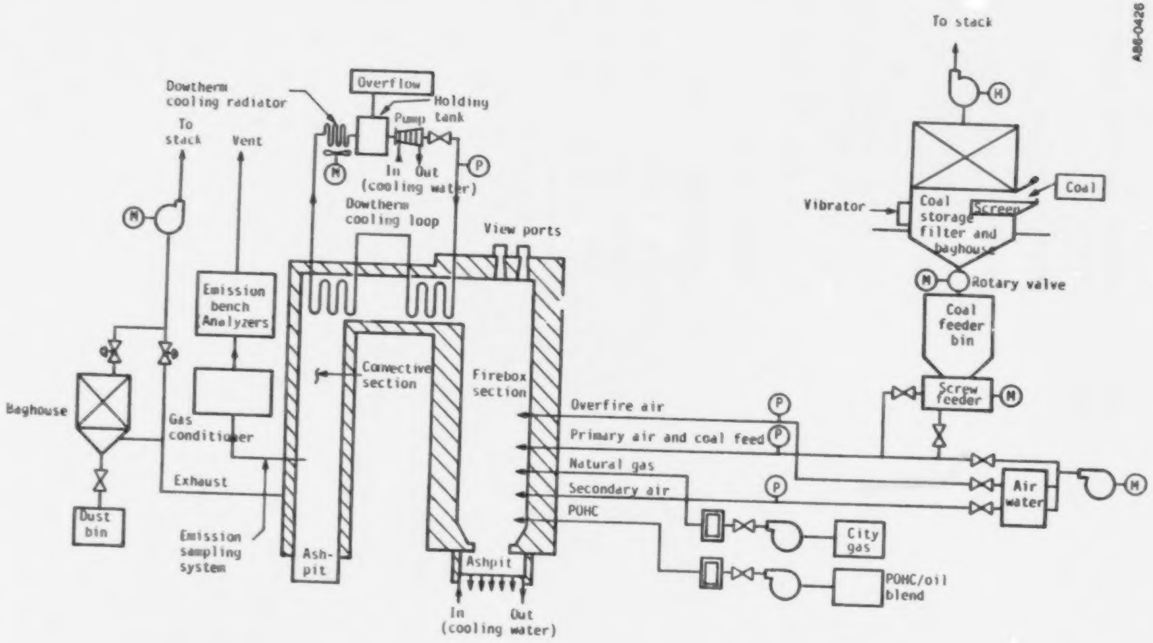
To stack
A86-0426
Dowtherm cooling radiator
Overflow
Holding tank
Pump
To stack
Vent
In Out (cooling water)
P
M
Dowtherm cooling loop
View ports
Vibrator
Coal storage filter and baghouse
Screen
Coal
Rotary valve
Coal feeder bin
Emission bench Analyzers
Convective section
Firebox section
Baghouse
Gas conditioner
Exhaust
Dust bin
Emission sampling system
Ash-pit
Ashpit
In Out (cooling water)
Overfire air
Primary air and coal feed
Natural gas
Secondary air
POHC
Screw feeder
Air water
City gas
POHC/oil blend

Figure 2. EPA Pilot-Scale Research Furnace System

bundle heat exchange drawers that are cooled to about 300°F with Dowtherm.

For oil firing, a 2.2-percent sulfur residual oil with heating value of 18,300 Btu/lb was used for the three burners fired on conventional fuel. The oil was heated to about 220°F by drum heaters and heat traced recirculation loops. For coal firing, an Illinois No. 6 coal with a 3.6-percent sulfur content was pneumatically conveyed to the burners.

The synthetic waste fired through the remaining burner was a blended mixture of 80 percent by weight No. 2 distillate oil, and 5 percent each carbon tetrachloride, trichloroethylene, monochlorobenzene, and trichlorobenzene. The mixture was recirculated continually with a pump to retard stratification, and fed to the steam atomized burner at room temperature. For baseline testing in the absence of waste, all four burners were fired on conventional fuel.

Thermocouples, sampling ports, and viewports are positioned along the furnace and convective section. Temperatures, flowrates, and emission measurements are recorded and processed on a microcomputer or data logger. Continuous monitoring was done for O_2, CO (two scales), CO_2, hydrocarbons, SO_2, and opacity.

Volatile waste constituents and PICs were sampled in the flue gas with the volatile organic sampling train (VOST). Two methods of using the VOST were used. For periodic comprehensive quantification, the full-VOST sampling protocol was used with GC/MS analysis following thermal desorption. To reduce the cost and turnaround time for multiple samples, a reduced protocol termed "miniVOST" was used. The sampling was done on a single VOST trap for 10 minutes and the trap was taken to a nearby gas chromatograph and desorbed to a parallel flame ionization detector and a Hall detector to quantitate hydrocarbons and chlorinated species, respectively. This procedure can provide near real time feedback on volatile organic waste concentrations.

Semivolatile wastes and products of incomplete combustion were sampled by a Modified Method 5 train fitted with an organics module containing 65 grams of XAD resin. The train was typically run for approximately 4 hours to a total sample volume of 4.3 dscm (150 dscf). The expended XAD was Soxhlet extracted along with other catches from the Method 5 and analyzed with the GC/MS.

TEST PROGRAM

To address the issues identified in the Introduction, seven test series were run as follows:

I	Baseline -- Fuel Only
II	Baseline -- Cofiring
III	Data variability, replication, and hysteresis
IV	Evaluation of high destruction efficiency operational window
V	Form and fate of trace metals
VI	Evaluation of PIC production
VII	Confirmatory tests

The Series I and II baselines were run to obtain reference levels of waste and PIC emissions under well controlled operation and for a clean test facility. Later runs as heat exchanger deposition increases will be compared to the baselines to determine possible background and hysteresis effects. This effect will be explored in Series III, where a sequence of volatile and semivolatile measurements will be compared to determine the background levels of waste and PICs and the reproducibility of the waste destruction efficiencies. With the data variability established and some calibration made on the confidence level, the remainder of the testing will be on obtaining a data base on waste emissions and PICs and the influence of operating conditions. Series IV will quantify the effect of off-design and upset operation on the high destruction efficiency window. Factors to be tested include low combustion air to the level of smoking and CO excursions; atomizer upsets; and flow or load transients. Additionally, wall cooling and lower residence times via capacity increases will be evaluated. In Series V, trace metals will be injected into the flame and the concentrations will be determined upstream and downstream of the baghouse as a function of particle size. Series VI will test the influence of waste identity on the concentration and identity of PICs. Inorganic chlorides will be used in place of the waste to determine if waste identity is dominant in PIC production. Finally, Series VII will test specific conditions found from the Series I to VI results to have a strong effect on waste or PIC emissions.

REFERENCES

1. Castaldini, C., et. al. "Engineering Assessment Report: Hazardous Waste Cofiring in Industrial Boilers," Final Report TR-84-159/EE on EPA Contract 68-02-3188, Acurex Corporation, Mountain View, California, June 1984.

TECHNICAL/ECONOMIC ASSESSMENT OF SELECTED PCB DECONTAMINATION PROCESSES

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ABSTRACT

Eleven emerging alternative treatments for Polychlorinated Biphenyl (PCB) contaminated sediments have been compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. In ranking the processes, weights were assigned the factors to emphasize the extent of decontamination, the estimated cost of treatment, and the versatility of the process. The emerging treatment processes are based on five different technologies: one on low-temperature oxidation, two on chlorine removal, one on pyrolysis, four on removing and concentrating, and three on microorganisms. Types of technologies not developed are chlorinolysis, stabilization, and enzymes. On the basis of the comparisons made, the treatment processes were ranked in the following order from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1 to 5 ppm) or less, with minimum environmental impacts and low to moderate cost. All the technologies except the advanced electric reactor required further development and testing.

INTRODUCTION

The PCB contamination problems in the Hudson River and New Bedford, Massachusetts are reported to be among the worst in the United States in terms of concentration and total quantity of PCB's. It is estimated that 290,000 kg of PCB's are contaminating 382,000 m^3 (500,000 yd^3) of sediments of the Hudson River. During the 70s, approximately 907,000 kg of PCBs were used in the New Bedford area annually, of which an estimated 45,500 kg were improperly disposed. The PCB contamination problems pose threats to both drinking water and the fishing industry. There are also numerous industrial lagoons contaminated with large quantities of PCBs.

The only available proven technology is dredging and expensive incineration. Land disposal of the sediments untreated has legal restrictions. Biodegradation is a possibility, but sufficient information does not exist to design and operate such a system. There is little experience in the application of encapsulation technology to PCB-contaminated sediments.

This study was undertaken to identify the most technically feasible processes that have been proposed by research concerns for the removal of PCBs from sediments; to identify their extent of development, effectiveness, limitations and probable costs; and to determine needs for further development. The study involved four phases: data acquisition, screening and selection of the most technically feasible processes, development of criteria for process assessment, and process assessment.

DATA ACQUISITION

Three major sources of data were: EPA's file of proposals and correspondence concerning problems of PCB contamination and possible approaches to alternative solutions; the open literature; and direct contacts with proponents of treatment technologies.

A bibliography (171 references) was prepared, which included treatment feasibility study reports, process test and evaluation reports, process development proposals, and patents. As processes were identified, direct contacts were made with the investigators for details of their process studies.

SCREENING AND SELECTION OF MOST TECHNICALLY FEASIBLE PROCESSES

Alternative destruction/detoxification/removal (DDR) processes were subjected to screening to identify those to be assessed further. The processes were categorized according to their generic technology so that their potential performance could be judged appropriately. Processes with undesirable aspects were rejected from further assessment. For example, lack of tolerance for water by a process is undesirable because extensive sediment drying is required. Processes showing insufficient tolerance for water were therefore rejected from further consideration as a primary treatment process in favor of more tolerant alternatives.

Table 1 lists the processes screened, identifies those selected for further assessment and gives the reasons for rejection of the rest. Some of the technologies (e.g. nucleophilic substitution) have provided several processes. Some (e.g. enzymes) have not yet provided any processes. A process evaluated as "1" in Table 1 was selected for further assessment. Other evaluation numbers assigned to the rest of the screened processes refer to footnotes that identify the reason for rejection of the process for further assessment. References cited are identified fully in the bibliography.

DEVELOPMENT OF CRITERIA FOR PROCESS ASSESSMENT

The PCB contamination problem in the Hudson River is representative of the type of PCB destruction/detoxification problems focused on in this study. It is expected that the contaminated sediments will have to be dredged from all sites and that the dredged sediments will have high water content.

Criteria for assessment of alternative treatments were chosen which relate to a broad range of principles of operation of diverse applied technologies, yet can be used effectively in comparing one treatment process with another. Additional factors, specific to a technology, were included to help portray the inherent strengths and limitations of a process. Table 2 lists the seven criteria used in comparative process evaluation and three additional factors relating to the needs for further process development and evaluation. The table also includes an overall description of the findings for the processes evaluated.

The goal set for process performance is to reduce the PCB concentration in treated sediments to levels of 1 to 5 ppm. Several of the processes were found to meet this goal. Those that showed reduction to less than 2 ppm were assigned a rating of "6". Those that attained a level between 2 and 10 ppm were assigned a "4". Those with residual concentrations greater than 10 ppm were rated "2".

Available capacity was found not to exist for any of the processes. However, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment. Those for which such projections could not be made were rated "2". Those requiring 24 or more months were rated "4". Those requiring 12 to 16 months were rated "6".

Conditions/limitations that were rated were tolerance for water, required processing time, and controllability of process conditions. Those treatments that could tolerate water up to about 40 percent would not require a drying step with its attendant fines' control problems. Those requiring only 1 day for treatment

TABLE 1. SCREENING OF PCB TREATMENT PROCESSES

Generic technology	References	Process	Evaluation[a]
CHEMICAL			
General	Centofanti 1971; Chen 1982; Childs 1982; Craddock 1982; Edwards et al. 1982; Environment Canada 1983; Hornig 1984; Massey and Walsh 1985; Rogers and Kornel 1985; Rogers 1983; Rogers 1985.		
Low-temperature oxidation			
Wet air oxidation	Baillod et al. 1978; Miller and Sevientoniewski (n.d.); Miller and Fox 1982.	Uncatalyzed, general	2
		Zimpro Process, Santa Maria, CA Weste Site	4,13
		Catalyzed	
		Dow Chemical Co. Patent 3,984,311	2
		IT Environmental Science`	2
Supercritical water oxidation	Modell et al. 1982.	Modar	1
Chemical oxidants	FMC Corporation (n.d.).	Potassium permanganate plus Chromic Acid and Nitric Acid	5
		Chloroiodides	4,7
		Ruthenium tetroxide	3,4,8
Ozonation	Arisman et al. 1981; Lacy and Rice Deschlaeger 1976; Prengle and Mauk 1978.	GE UV/ozonation process	2
Chlorine removal	U.S.P. 4,469,661	Molten aluminum/distillation	14
Dehydrochlorination	Chu and Vick 1985; Lapiere et al. 1977.	Catalytic:	2,3
		Nickel on kieselguhr	2,3
		Pd on charcoal	2,3
		Lithium aluminum hydride	2,3
		Butyl lithium	2,3
		Raney Nickel	2,3
Reducing agents	Chu and Vick 1985; Sworzen and Ackerman 1982.	Sodium in liquid ammonia	7,9
		Nickel-catalyzed zinc reduction	7,9
		Hydrazine	7,9
		UV light plus hydrogen	2
		Mildly acidic zinc powder, Sweeney and Fisher (1970)	2,14
Nucleophilic substitution	Brown et al. 1985a; Brunelle and Singleton 1985; March 1968; New York University 1984; Ruzz et al. 1985; Smith and Gurbacham 1981; Sunohio (n.d.); Sweeny and Fischer 1970; United States Patent Office 1984b; Weitzman 1984; Weitzman 1984; Weitzman 1985.	Sodium-based processes:	
		Goodyear, sodium in naphthalene (1980)	10
		Acurex, proprietary solvent	10
		PCBX/Sun Ohio	10
		PPM	10
		Ontario Hydro Power	10

(continued)

TABLE 1 (continued)

Generic technology	References	Process	Evaluation[a]
Nucleophilic substitution (continued)		Potassium poly (ethylene glycolate) based:	
		EPA In-house KPEG	19
		KPEG Terraclean-C1	1
		GE KOH-PEG	11
		New York University KPEG	12
Radiant energy	Bailin and Hertzler 1977; Bailin and Hertzler 1978; Bailin et al. 1978; Craft et al. 1975; Dev et al. 1985; Kalmaz et al. 1981; Meuser and Weimer 1982; Plimmer 1978; Rogers and Kornel 1985; Rogers 1985; Trump et al. 1979; West et al. 1983.	UV/photolysis	3
		Syntex photolytic	3,4
		Thermal corona glow	5
		Microwave plasma	9,17
		RF insitu heating	18
		Gamma radiation (Craft et al. 1975)	9
		LARC	1
Electromechanical reduction	Massey and Walsh 1985.	Electromechanical research process	14
Chlorinolysis	Sworzen and Ackerman 1982.	Hoechst process	9
		Goodyear catalytic hydrogenolysis	9
		Exhaustive chlorination	9
Pyrolysis	Boyd 1985; New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b.	Advanced Electric Reactor	1
		Wright-Malta alkaline catalyst fuel-gas process	12
PHYSICAL			
Removing and concentrating	Angiola and Soden 1982; Caron 1985; Gilmer and Freestone 1978; Githens 1984; Hancher et al. 1984; Hawthorne 1982; Lee et al. 1979; Saunders 1985; Schwinn et al. 1984; Versar, Inc. 1984.		
Heated Air Stripping		American Toxics Disposal, Inc.	14
Extraction		Critical Fluid Systems, CO_2	14
		Furfural	15
		Acurex solvent wash	1
		O. H. M. extraction	1
		Soilex process	1
Adsorption		Carbon adsorption, general	13
		Neoprene rubber adsorption	15
Vitrification	Timmerman 1985.	Battelle vitrification process	1

(continued)

TABLE 1 (continued)

Generic technology	References	Process	Evaluation[a]
Stabilizing	Ghassemi and Haro 1985; Law Engineering Testing Company 1982; Stroud et al. 1978; Subnamanian and Mahalingam 1977; Tittlebaum et al. 1985.	Asphalt with lime pretreatment	16
		Z-Impremix	15
		Sulfur-asphalt blends (K-20)	16
		Ground freezing	13
Bottom recovery	Carich and Tofflemire 1983; Hand and Ford 1978; Murakami and Takeishi 1978; U.S. Army Corps of Engineers Water Resources Support Center 1983; Zimmie and Tofflemire 1978.	Dredging	13
BIOLOGICAL			
Microorganisms	Bedard et al. 1985; Bumpus et al. 1985; Clark et al. 1979; Dawes and Sutherland 1976; Furakawa 1982; Isbister et al. 1984; Kong and Sayler 1983; McCormick 1985;	Bio-Clean	1
		Sybron Bi-Chem 1006 PB	1
		Composting	1
		Bio-Surf	4,13
	New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b; Rhee et al. 1985b; Rhee et al. 1985; Unterman et al. 1985.	Ecolotrol, Inc.	4,13
		Wormes Biochemical's Phenobac	11,13
		Rhee anaerobic degradation	14
Enzymes	Catelani et al. 1971; Rochkind et al. Unterman et al. 1985.	No processes found	

[a] Explanation of process rating:

1. Identified emerging sediment treatment process.
2. Destruction efficiency appears to be too low to meet environmental goals.
3. Processing time appears to be extremely long for practical timely cleanup.
4. Data available for dioxin, other chlorinated compounds, or other contaminants, but not PCB's.
5. Process has been shown to destroy PCB's in gas streams only. It may be feasible for sediments, but has not been shown to be.
6. PCB's with 5-7 chlorine atoms per molecule are not destroyed.
7. Products of partial degradation may be toxic.
8. Reagent is very costly/toxic or both.
9. Process costs appear to be excessively high compared with other emerging treatment processes.

10. Water destroys the reagent or interferes with its action, thus the process would require excessive drying of sediments and, probably, extraction in pretreatments. The process would therefore have application only as a subordinate final step to several extraction and concentration operations.

11. This particular process was not evaluated because data were not available for assessment.

12. This process is an alternative to another process using the same generic technology, but it is in very early stages of development, and data were not available for assessment.

13. This technique is basically applicable to preliminary operations prior to treatment or to treatment of wastestreams (e.g., wastewaters) from chemical or physical treatments.

14. This process is in the concept stage and data are insufficient to assess it for PCB-contaminated sediments.

15. This process has been found to be ineffective.

16. This technology provides only for encapsulation of the PCB-contaminated sediments.

17. This process supports incineration of PCB's.

18. The process does not appear to be feasible for submerged sediments.

19. Basic data support to identify emerging treatment process.

TABLE 2. CRITERIA AND TECHNICAL FACTORS USED IN PROCESS ASSESSMENT

Criteria/Factor	Description
Criteria	
Estimated Residual PCB	The goal set for process performance was to reduce the PCB concentration in treated sediments to levels of 1 to 5 ppm. Several of the processes were found to meet this goal.
Available Capacity	Although available capacity was found not to exist for any of the processes, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment.
Conditions/Limitations	These included tolerance for water, required processing time, controllability, extent of destruction/decontamination, number of stages of extraction required, and limits on the concentration of PCBs that could be treated. Some processes required one day or less for cleanup; some biological processes required more than 3 weeks.
Concentration Range Handled	The PCB concentration of the sediments treated ranged from unknown to 3000 ppm. Some processes had limits inherent in the technology.
Status of Development	Processes were found to range from concept stage to completed field test stage. Most were in the pilot stage of testing.
Test and Evaluation Data Needs	Data needs varied with the status of the process development. At worst, data were available showing tests of the concept. At best, the process had been field tested, and only permits and checkout were needed.
Estimated Cost	The estimated costs of treatments were made in terms of the cost per cubic meter of dry sediment treated, assuming a density of 1.68 Mg/m^3, plus costs of associated operations-dredging, transportation, handling of treated sediments, as required. All costs are stated in 1985 dollars.

(Continued)

TABLE 2. (Continued)

Criteria/Factor	Description
Factor	
Unit Operations	The process technology was described, including the active agents, the principles and mechanisms of PCB destruction, and complete characterization of all unit operations.
RCRA Waste Generated	Some processes have hazardous wastes as residuals from the treatments applied.
Estimated D/D/R Efficiency	All the processes achieved a better than 90% destruction/detoxification/removal (D/D/R) efficiency.

could generally show a faster rate of cleanup than those requiring 3 days. Some biological processes required more than 3 weeks. The treatments generally provided control of the processing conditions; however, a few (e.g., composting) would not necessarily do so. The three conditions/limitations were ranked as follows:

Conditions/limitations	Rank
Tolerates to 40 percent water and treats in 1 day	6
Sediment needs to be dried	5
Tolerates to 40 percent water and treats in 3 days	4
Tolerates water and treats in >3 weeks	3
Sediment needs to be dried, treats in >3 weeks	2
Processing conditions uncontrollable	1

Concentration range handled in data developed for the processes ranged from unknown to 3,000 ppm. Ratings were assigned based on the upper limit of feed concentration. The ratings were as follows:

PCB concentration treated, ppm	Rank
≥3,000	6
2,000 to 3,000	5
1,500 to 2,000	4
500	3
250 to 350	2
Unknown	1

Status of development ratings were "1" for no data, "2" for laboratory-scale tests completed, "3" for bench-scale tests completed, "4" for pilot-scale tests completed, "5" for field tests completed; and "6" for commercial system designed and ready for construction.

Test and evaluation data needs could be rated differently, depending upon the purpose. For indicating the extent to which a treatment process is readied for use, the more data that are available the better. For indicating the need to support a very promising technology that lacks sufficient progress, the potential and the data needs should be rated in combination. The ratings used here are for the former purpose and are as follows:

Test and evaluation data needs	Rank
None except permits and checkout	6
Field tests	5
Pilot tests and costs	4
Laboratory and bench tests	3
Conceptual treatment process design	2
D/D/R data, residual PCB data, RCRA waste data	1

The application of any treatment process can involve the need for one or more of the following unit operations: dredging, transport, storage, landfill disposal, land treatment disposal, incineration, and/or alternative treatment. Estimates were developed for all of these so that, in any given process evaluation, the proper elements could be added to obtain an estimate of the cost of application. The estimates were made in terms of the cost per cubic meter of sediment treated. The sediment was assumed to have a density of 1.68 Mg/m^3.

Dredging costs for those treatments requiring removal of the sediment before treatment are estimated at \$20/m^3 based on the recent experience of the U.S. Army Corps of Engineers in contracting for dredging in the New York State area (Wheeler, 1986).

Transport costs are given as a range. The Corps' experience is \$13/m^3 for short hauling distances (Wheeler, 1986). A cost of \$126/m^3 was used for long hauling distances, which represents an assumed 483-km average transport distance to RCRA landfills capable of accepting PCB-contaminated wastes (Industrial Economics, Inc., 1985).

Storage cost will sometimes be incurred to hold the dredged sediments pending treatment; e.g., where dredging rates exceed the rates at which the treatment can be applied. These have been set arbitrarily at \$10/m^3.

Land treatment was used in one of the processes to degrade residual solvent left in the soil after treatment. This involves the controlled application of wastes to the surface of the soil. At land-treatment facilities, wastes are either spread on or injected into the soil, followed by tilling into the soil with farm equipment. The physical and chemical properties of the soil, in unison with the biological component of the soil and sunlight work together to immobilize, degrade, and transform portions of the wastes. The application and tilling process can be repeated many times on the same plot, making land treatment a dynamic system designed to reduce and ultimately eliminate a portion of the waste, as opposed to permanent storage such as landfills.

The American Petroleum Institute (1983) has reported that there were 213 land-treatment facilities in operation handling waste from 16 different industry sectors. The most extensive use of land treatment is for petroleum refinery wastes, with 105 land-treatment facilities, many of which are located on the same site as the refinery. More recently, EPA verified the existence of 114 land-treatment facilities and obtained information on operating parameters at some of these sites (Thorneloe, 1986).

Wastes are typically mixed to a depth of 0.5 to 1.0 feet, where biochemical reactions take place. Application frequencies can range from daily to yearly, with tilling occurring as frequently as daily.

The average cost of controlled, managed land treatment cited by the American Petroleum Institute, \$60/ton, equates to \$111/m^3 of sediments. For short-term land treatment of readily-degradable solvents remaining in treated sediments free of PCBs after they are washed or dried, the cost is estimated at \$33/m^3 (Caplan, 1986).

Redeposition costs of decontaminated sediments were also estimated at \$33/m^3. Slightly lower costs might be expected in special cases.

Because the regulations permit the use of incineration or chemical waste landfill and the application costs of these two methods are available from firms engaging in their practice, these costs were used as lower and upper limits with which to compare the costs of applying new alternative technology.

Landfill disposal costs, incurred when the sediments must be placed in authorized chemical waste landfills, are estimated as ranging from \$260/m^3 for the Michigan area (EPA Regional Office) to \$490/m^3, based on the highest prices charged for hazardous wastes by commercial facilities (Industrial Economics, Inc., 1985). This range includes an intermediate value of \$420/m^3 reported by the Corps of Engineers.

Costs for incineration techniques capable of achieving 99.9999 percent destruction and removal efficiencies for PCBs are difficult to predict. Even more difficult is prediction of the price commercial facilities will charge to accept the responsibility of handling such a sensitive waste. Surveys made to determine the likely charges to incinerate dioxin-containing wastes resulted in a reported price on the order of \$1,000/Mg (Pope-Reid Associates 1985). This translates to \$1,680/m^3, the value adopted for this evaluation, and the cost of disposal of residue from incineration is included. The total cost of use of incineration including dredging at \$20/m^3 and transport at \$13 to \$126/m^3 is \$1713 to \$1826/m^3.

When available, alternative treatment costs were obtained from the proponent of the process. Otherwise, they were estimated based on the types of unit processes involved and the environmental controls required, or they were determined not to be estimable considering the status of development of the process.

While all costs are in 1985 dollars, the treatment costs are not all necessarily based upon the same labor rates, corporate fixed charges, or profit. These costs vary from one firm to another. The cited estimates are costs of purchasing the treatments. Further cost analyses will be needed to provide a basis for comparison of processes on the basis of individual cost elements.

Table 3 shows the unit cost estimates used to develop cost ranges for the emerging treatments.

Estimated costs were rated by comparing the range of the cost estimates

TABLE 3. UNIT COST ESTIMATES FOR STEPS INVOLVED IN TREATMENT AND DISPOSAL OF PCB-CONTAMINATED SEDIMENTS

Operation	Cost, $/m^3
Dredging	20
Transport	13 to 126
Storage	10
Landfill and Disposal	260 to 490
Landfarming	33
Restricted Land Disposal	111
Incineration	1680

obtained with the cost of placing them into a chemical waste landfill. Treatment processes showing the lowest estimated cost range were rated "6"; those showing a probable cost lower than landfill were rated "4"; those showing an estimated cost equal to landfill were rated "2"; and those showing an estimated cost range greater than landfill were rated "1".

Overall ranking was accomplished through the use of weighting factors assigned to each rated factor. The weighted average rank was then obtained by summing the products of the weighting factors and the ratings and dividing by the sum of the weighting factors. The weighting factors were:

Factor	Weight
Residual PCB concentration	5
Capacity	2
Conditions/limitations	3
Concentration range handled	2
Status of development	2
Test and evaluation data needs	1
Estimated costs	4

The weightings tend to give greatest emphasis to the ability of the treatment to reduce the PCBs and to the probable cost of the treatment. Much less emphasis is placed on the status of development. Thus, an almost fully developed process with an extremely high cost would be ranked lower by application of the weighting process than a less developed process with a much lower potential cost. Test and evaluation data needs have not been heavily weighted because nearly all the alternative treatment processes that show low potential cost require more data to be proven.

Under this procedure, the perfect process for treating PCB-decontaminated sediments would show the following levels for each ranking factor and would receive, using the ratings given, a weighted rating of 6.0:

Factor level	Rating, R	Wt	R x Wt
1. Residual PCB, treated sediment less than 1 ppm	6	5	30
2. Capacity adequate for site cleanup available in 12-16 mo.	6	2	12
3. Tolerates to 40 percent water and treats in 1 day (24 hr)	6	3	18
4. Handles concentrations greater than 3,000 ppm	6	2	12
5. Commercial system designed and ready for construction	6	2	12
6. No test and evaluation data needs except permits and checkout	6	1	6
7. Lowest estimate cost range among alternative emerging technologies	6	4	24
Total R x Wt	Σ R x Wt		114
Weighted rating (Σ R x Wt)/ΣWt			6

PROCESS ASSESSMENT

The processes were assessed by characterization and ranking. Characterization provided for objective comparison of the processes. Ranking provided a subjective comparison of the processes based on the seven criteria.

CHARACTERIZATION

Table 4 summarizes five characteristics of the processes: unit operations, available capacity, conditions/limitations, concentration handled, and any generated RCRA wastes. The unit operations employed are given, and each is identified by a number. Generally, a greater number of unit operations will mean a greater effect on treatment costs.

TABLE 4. TREATMENT PROCESS ASSESSMENT

Process	Unit operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
Chemical					
Supercritical water oxidation	1,4,10	—	20-40% solids; 374 °C, 23.3 MPa organic content >5% or supplemental fuel	>3000 ppm	None
KPEG, Terraclean-CL	1,3,4,7	(24 mo)	150 °C, 0.5-2 h	500 ppm or greater	w.w.tr. act. carbon
KPEG, NYU	1,2,3,4,5, 6,7,9	—	—	—	—
KPEG, EPA in-house	Basic process data				
LARC	1,2,5,15,	(24 mo)	tolerates 25% water.	480 ppm	None
Advanced electric reactor (I.M. Huber)	7,8,12,13 14	(16 mo)	2204 °C, 2,400 kWh/m^3 needs predryer	>3000 ppm	None
Physical					
O. H. Materials methanol extraction	2,7,8,14 15	—	predry to <1% moisture	>400 ppm	PCB-loaded carbon from solvent cleanup
"Soilex" kerosene/water	1,2,5,15	—	25% of kerosene solvent retained in soil; 3 d per batch	to 350 ppm tested	Concentrated PCB from still to incineration
Acurex solvent wash	2,4,5,6, 10,11	—	3-12 washes, tolerates <40% water.	up to 1,983 ppm	Concentrated PCB's to KPEG
Vitrification	8,12,14	—	Electrical power usage increases with soil moisture; submerged sediments dredged and treated	500 ppm	None

(continued)

TABLE 4 (continued)

Process	Unit operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
Biological					
Composting	15,16	(16 mo)	Seasonal effects, reaction time must be >4 weeks	1,590 ppm	Treated material is still a RCRA waste
Bio-Clean	1,2,17	27 m^3/d available, 12 mo for full-size	Proved for PCP, laboratory confirmed for PCB's	≤300 ppm	None
Sybron Bi-Chem 1006	15,17	—	Unknown	Unknown	Unknown

NOTE—Unit operations key:

1. Liquid/solids separation
2. Extraction/solubilization (liquid-solids)
3. Liquid/liquid extraction
4. Chemical reactor
5. Stripping still
6. Solvent recovery still
7. Adsorption
8. Dryer (solids)
9. Dryer (liquids)
10. Filtration
11. Steam cleaning
12. Thermal reactor
13. Grinding
14. Air pollution controls
15. Landfarm
16. Innoculation/digestion
17. UV light reactor

None of the processes has currently available capacity approaching that required for major cleanups. Therefore, the time required to build capacity is listed. Construction time ranges from 12 to 24 months.

Certain conditions that typify the process or limit its versatility are given in column 4 of Table 4. Table 4 also identifies any RCRA waste streams generated by the process.

The data from studies of the processes were examined for ranges of PCB concentrations handled to date. Generally, the values are not limitations on the process, but only on the data acquired. The value ≤300 ppm for the Bio-Clean process may, however, be a limitation requiring process adjustment to control.

Table 5 lists five additional characteristics of the processes and the rating developed in the ranking process. The characteristics shown here relate to the needs for further process development and evaluation. The process status is given in terms of stages of development completed. The processes range in stages completed from concept to pilot plant.

Both PCB destruction and residual PCB concentration in treated sediments are given to the extent available. Certain processes may require extension of the unit operations, employed (e.g., more stages of extraction) to attain the required performance levels.

Test and evaluation data needs are indicated for each process. Needs vary from none (AER process) to complete site-specific evaluation.

The estimated costs of applying the process are listed in $\$/m^3$. Although cost estimates lack the necessary accuracy at this stage of development of the alternative processes to serve as the sole criterion of potential, they nevertheless indicate that seven of the processes may cost no more than landfill and five could cost less. (Cost estimates could not be made for the Sybron process and composting.)

The processes varied in complexity as evidenced by the number of unit operations employed. Supercritical water oxidation, Bio-Clean and vitrification each employed three unit operations; KPEG employed eight. Operator training requirements were not evaluated comparatively due to insufficient data. However, for the scaled-up treatment processes, the operating labor requirements are expected to be quite similar.

RANKING OF TREATMENT PROCESSES

In contrast to process characterization which involves all factors listed in Tables 4 and 5, ranking is subjective and is based on the seven criteria previously described. An attempt was made to define and determine a single number that could represent the overall position of each process relative to an arbitrarily defined perfect process.

Based on the weighted ratings, the processes rank as follows from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006 PB/Hudson River Isolates.

CONCLUSIONS

Emerging treatment processes for decontamination of sediments containing PCBs that show potential as alternatives to incineration and chemical waste landfill have been identified. Eleven alternative treatments were compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1-5 ppm) or less, with minimum environmental impacts and low to moderate cost. The sediments must be dredged for application of these treatments.

Of the eleven processes assessed, all but the Advanced Electric Reactor (AER) are in various stages of development from laboratory-scale through field tests. The AER is a permitted treatment under TSCA in EPA Region VI, based on completed trial burns. There is no immediately available capacity for any of the treatment processes. Further data are needed in most cases to define the final system designs for the processes.

TABLE 5. TREATMENT PROCESS ASSESSMENT

Process	Status[a]	Estimated D/D/R efficiency, %[b]	Estimated residual PCB, ppm	Test and evaluation data needs	Estimated costs, $/m^3	Rating[c]
Chemical/physical						
Supercritical water oxidation, Modar	Field test with PCB liquids	>99.9995	<0.1 ppb	1,2,3,4,5,6,7,	250-733	4.58
KPEG Terraclean-CL	Pilot tests	>98	<1 ppm	1,6	208-375	5.42
LARC	Lab tests	>90	38-50	2,3,4,5,6,7	223-336	5.26
Advanced electric reactor	Pilot tests	>99.9999	<1 ppb	None[d]	830-943	4.58
Physical						
O. H. Materials, methanol extraction	Field tests under way	97	<25 ppm	2,3,6,7	401-514	4.16
Soilex	Pilot tests	95 (3 stages)	6-9 ppm	5,6,7	856-913	3.26
Acurex solvent wash	Pilot-scale (field tests planned)	e	<2 ppm	Identity of mixed solvent, 6,7	196-569	5.21
In-situ vitrification Battelle Pacific NW for EPRI	Pilot test of soil	99.9	None in vitrified block, 0.7 ppm in adjacent soil	6	255-548	4.53

See footnotes at end of table.

(continued)

TABLE 5 (continued)

Process	Status[a]	Estimated D/D/R efficiency, %[b]	Estimated residual PCB, ppm	Test and evaluation data needs	Estimated costs, $/m^3	Rating[c]
Biological						
Composting, aerobic	Lab-scale	62	504-908	4,5,6	—	2.47
anaerobic	Lab-scale	18-47	825-1268	4,5,6	—	2.47
Bio-Clean, aerobic	Bench-scale	99.99	25 ppb	3,5,6,7	191-370	4.84
Sybron Bi-Chem 1006	Lab-scale and concept	50	—	3,4,5,6,7	—	1.48

NOTE--Data needs key:

1. D/D/R data
2. Residual PCB data
3. Unit operations data
4. Bench-scale data
5. Pilot-scale data
6. Field test data
7. Cost data
8. RCRA waste

[a] Status is defined in terms of the types of studies completed.

[b] D/D/R = destruction/detoxification/removal.

[c] The rating was obtained as shown by the example, under Characterization.

[d] AER is fully permitted under TSCA in EPA Region IV for destruction of PCB.

[e] Treatment is continued until a residual of <2 ppm PCB's is obtained.

At this stage, estimated costs of application of these eleven processes are less than or within the range of costs of chemical waste landfill, except for the AER estimated cost, which exceeds that of landfill, but is less than incineration. These costs are planning estimates only. In most cases, further research is needed to provide data suitable for more definite cost estimates.

The emerging treatment processes are based on six types of generic technologies: low-temperature oxidation, chlorine removal, pyrolysis, removal and concentration, vitrification (melting), and microorganisms. Types of generic technologies not yielding competitive emerging processes are: chlorinolysis, stabilization, and enzymes. A search of these technologies yielded no suitable candidate processes at this time.

On the basis of the comparisons made, the treatment processes were ranked in order, from highest to lowest, as shown in Table 6. The estimated cost range (1985 dollars) per cubic meter of sediment treated is also shown for each process. Costs of chemical waste landfill and incineration are given for comparison.

NOTICE

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TABLE 6. SUBJECTIVE RANKING OF TREATMENT PROCESSES ON OVERALL SUITABILITY, AND ESTIMATED COST OF APPLICATION

Process	Cost of application, $\$/m^3$ treated
KPEG	\$211-378
LARC	\$223-336
Acurex Solvent Wash	\$196-569
Bio-Clean	\$191-370
Modar Supercritical Water	\$250-733
Advanced Electric Reactor	\$830-942
Vitrification	\$255-548
OHM Methanol Extraction	\$400-514
Soilex Solvent Extraction	\$856-913
Composting	Unable to estimate cost
Sybron Bi-Chem 1006	Unable to estimate cost
Chemical Waste Landfill	\$260-490
Incineration	\$1713-1826

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MOBILE KPEG DESTRUCTION UNIT FOR PCBs, DIOXINS AND FURANS IN CONTAMINATED WASTE

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ABSTRACT

The presence of highly toxic and persistent chemicals in liquids, soils, sediments, and sludges in abandoned waste sites poses a threat to both public health and the environment. Incineration is frequently used to destroy highly hazardous wastes, however, when operated under less than optimum combustion conditions acutely hazardous products including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) can be formed and emitted in the combustion products. Various biological, chemical, and physical methods have been tested and have been demonstrated to be effective to varying degrees in destroying halo-organics.

The U. S. Environmental Protection Agency (EPA) has supported research intramurally and extramurally since 1980, to develop an alternative method for in-situ or on-site destruction of halogenated pollutants. Chemical reagents prepared from polyethylene glycols and potassium hydroxide (KPEGs) have been demonstrated under mild conditions (25°-140°C) to dehalogenate PCDDs and PCDFs to less than 1 ppb of starting materials. The reaction mechanism is nucleophilic substitution at an aromatic carbon.

Toxicological tests have established that arylpolyglycol by-products from KPEG reactions are non-toxic. In July and August, 1986, a 2700 gallon KPEG reactor was used in Butte, Montana and Kent, Washington to successfully destroy PCDDs and PCDFs (120 ppb - 200 ppm) in 17,000 gallons of liquid waste to non-detectable levels. A new 2 cubic yard KPEG reactor designed to treat both liquids and soils will be field tested in 1987.

INTRODUCTION

The accumulation of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs, "dioxins") in soil, sediment, and living tissue is a serious problem that has received considerable public attention in recent years. As an example, there existed in 1982 an estimated 415 commercial wood-preserving plants in the U.S. generating daily a total of nearly 5.5 million gallons of process waste which contained toxic materials (1). The pentachlorophenol (PCP) products purchased by industry to treat wood normally contain 100-200 ppm heptachlorodibenzo-p-dioxin (HpCDD) and 1000 to 25000 ppm octachlorodibenzo-p-dioxin (OCDD). Also, preliminary investigations of dioxins showed that in the use of PCP with these high concentrations of HpCDD and OCDD, and with the high temperatures and pressures involved, there existed the possibility that the more toxic tetrachlorinated dioxins and furans might be formed. Of the disposal options available, the majority of the wood preserving plants practiced storing the waste water on site, relying on evaporation to reduce liquid waste to sludge.

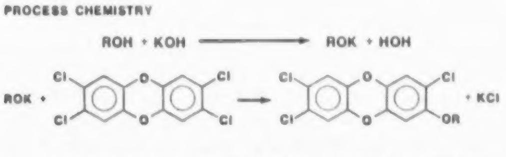
Conventionally, the "clean up" of such contaminated sites usually involves landfilling and is not really a permanent solution but rather a transfer of a toxic waste from one region to another. Landfilling will be curtailed in 1988 under the 1984 RCRA amendments.

The chemical stability of PCDD, PCBs and other haloorganics precludes their destruction by conventional refuse incineration methods. Most municipal incinerators cannot achieve the high temperatures necessary to destroy these chemicals. Mobile incinerator technology has been developed for on-site treatment of waste, however, early estimates are that on-site incineration of toxic waste at a wood preserving site will be costly.

CHEMICAL PROCESS

Chemical decontamination is an alternative to thermal processing or landfilling of soils contaminated with PCDDs or other aromatic halides such as chlorobenzenes or PCBs. Chemical decontamination, like incineration, involves changes to the chemical structure of the dioxin molecule. While chlorinated dioxins are thermally stable, they readily dechlorinate to water soluble compounds under relatively mild conditions of temperature and pressure. For example, chlorinated dioxins in oil are readily reduced to the parts per trillion level within 15 minutes at 80°C by reacting them with a compound which is not oil soluble. In soils processing, the PCBs and PCDDs are dechlorinated to a water soluble form which will remain with the soil or be contained in the reagent that is recovered for reuse. Dechlorination also affects the toxicity of the dioxin, with dioxins containing fewer than three chlorine atoms generally showing low toxicity (2).

The proposed mechanism for these reactions is shown in the following example using 2,3,7,8-tetrachlorodibenzo-p-dioxin:



An alkali metal hydroxide, usually potassium hydroxide (KOH) is reacted with an alcohol or glycol such as polyethylene glycol 400 (PEG 400) to form an alkoxide. The alkoxide (RO^-) reacts with one of the chlorine atoms on the chlorinated dioxin to produce an ether and the alkali metal salt. This dechlorination may proceed to complete dechlorination, although replacement of a single chlorine is sufficient to make the reaction products water soluble.

TOXICITY CONSIDERATIONS

A major concern in this type of processing involves the toxicity of any reagents and/or reaction products which may be left in the decontaminated matrix after treatment. Some toxicity data on reagents used in the process are shown in Table 1, along with comparison values for sodium chloride and 2,3,7,8-TCDD. The reagents used in this process are some five times less toxic than table salt, and roughly six orders of magnitude less toxic than 2,3,7,8-TCDD, the dioxin isomer of major concern. Polyethylene glycol 400 is an FDA approved material for use in foods and cosmetics.

Toxicity testing of the reacted aromatic halides were conducted in EPA's Research Triangle Park and Duluth laboratories. Structural assessment of the theoretical toxicity of the reaction products is favorable, i.e., the known reaction products would not be expected to show significant toxicity. Results of the Ames test for mutagenicity are negative, i.e., the reaction products do not demonstrate carcinogenic potential. Bioaccumulation tests also produced negative results, which is not surprising given the water solubility of these reaction products (3,4).

In earlier LD_{50} studies conducted by the EPA Duluth laboratory and others, it was demonstrated that 2,3,7,8-TCDD is extremely toxic to fish, producing mortality in carp at water concentrations

TABLE 1. TOXICITY OF REAGENTS AND COMPARISON MATERIALS

Material	LD_{50}, Oral-rat(3)
polyethylene glycol 400	27,500 mg/kg
sodium chloride (comparison value)	3,000 mg/kg
2,3,7,8-TCDD (comparison value)	0.022 mg/kg

as low as 60 ppq (5,6,7,8). By analyzing tissue residue levels of TCDD in these carp and expressing the results as ug accumulation dose/kg body weight, it was possible to make a rough comparison between these results and mammalian studies investigating TCDD. These comparisons indicate that carp are approximately as sensitive to TCDD as guinea pigs. (LD_{50} 600 ng/kg body weight.)

In LD_{50} tests 5.8 mg of by-products from the KPEG-TCDD reaction was injected into a 40 liter aquarium containing 15 carp. This resulted in a nominal water concentration of 250 ppt of reacted TCDD (3). In a previous study conducted under similar conditions except at a measured water concentration of 60 ppq TCDD, carp showed gross pathological damage. These damages included cranial deformation, lateral line lesions, fin darkening, hemorrhages and ulceration of the ventral body wall (5,6). The absence of mortality and gross pathological damage in exposures to KPEG-TCDD adducts concentrations more than 4000-fold greater than those in the previous study lead to the conclusion that treatment of TCDD with KPEG changes it to a non-toxic form or at least reduces its toxicity by several orders of magnitude (3). The non-toxic properties of KPEG reaction products improves the prospects of on-site treatment, delisting and disposal of haloorganic contaminated materials.

FIELD TESTS

Studies were initiated in January 1986 to determine if KPEG could be used to treat PCDD and PCDF contaminated oil at a wood preserving industrial site near Butte, Montana. The wood preserving site contained approximately 9000 gallons of light petroleum oil collected previously from groundwater over a period of two years. The oil contained 3.5% pentachlorophenol, PCDD and PCDF homologs ranging from 422 ppb of tetrachlorinated isomers to 83,923 ppb of octachlorinated isomers. Because of the presence of these highly toxic chlorinated dioxins and furans, the oil could not be transported off-site for incineration. Bringing in and operating a mobile incinerator for on-site destruction of contaminated oil was rejected because of high costs.

In April 1986, U.S. EPA Region 8 agreed, after review of laboratory data, that the chemical process, based upon a KPEG reagent, could be used to decontaminate on-site the PCDD/PCDF contaminated oil.

Initial treatment experiments with some of the PCP waste-contaminated samples obtained from Butte, Montana were accomplished on January 9, 1986. For these tests, two 500-ml samples were obtained, one an oil waste and the other a contaminated soil. The procedures utilized for the treatment of the oil samples with the KPEG reagents are described in the following:

- ° Two aliquots of oil samples (24.94 grams) were removed from the container and accurately weighed into new, pre-cleaned 125-ml sample bottles fitted with Teflon-lined caps. A reagent blank bottle was simultaneously prepared.
- ° Twenty-five (25) grams of the KPEG reagent were added, at ambient temperature, to each of the three sample bottles mentioned above.
- ° The bottles were placed in sand baths maintained at temperatures of 70°C and 100°C for a period of 8 hours and the contents of each bottle were stirred with a motor-driven stirring rod during this entire period.
- ° Accurately weighed aliquots (typically 1-5 grams) of the sample were removed from the reactor at intervals of 15 minutes and placed in 125-ml flint glass bottles. The destruction reaction which had been occurring was quenched by adding a sufficient quantity of 50% H_2SO_4 to each bottle to adjust the pH to about pH 7, as determined by indicator paper.

Following quenching of the treated samples, the bottles were set aside until test portions could be successfully extracted and analyzed (9).

The procedures for extraction and analysis of PCDD and PCDF were based on adding appropriate internal standards to each aliquot taken from the reaction. At a minimum, 1-2 ng each of 2,3,7,8-[$^{13}C_8$]-TCDD, 2,3,7,8-[$^{37}Cl_4$]-TCDD and 2,3,7,8-TCDF were added to each 125-ml flint glass bottle containing 1-5 grams of the treated oil sample. Sample extracts were prepared and were analyzed using DB-5 capillary GC columns to obtain data on the concentrations of PCDDs and PCDFs. Perkin-Elmer Sigma II or Varian 3740 GCs were used for the analysis. The Kratos MS-30 Mass Spectrometer was used in the low resolution mode to detect PCDDs and PCDFs. If PCDDs and PCDFs were detected, a second portion of the sample extract was analyzed using high resolution MS (9).

RESULTS

The oil samples obtained from the Butte, Montana site were treated as described with KPEG and were analyzed by GC MS to determine if PCDDs and PCDFs had been destroyed, as required by the regulation, to less than 1 ppb. Table 2 shows that many of the congeners of PCDD and PCDF were destroyed effectively by the KPEG with a temperature as low as 70°C for 15 minutes. All PCDD and PCDF congeners were completely destroyed by KPEG when the sample was heated to 100°C for 30 minutes. As a result of the successful laboratory tests, arrangements were made to lease equipment to treat the remaining oil stored on the site (10).

The field equipment used to process the oil consisted of a 2700-gallon reactor mounted on a 45-foot trailer equipped with a boiler, cooling system, a laboratory and a control room. Heating of the oil and reagent was achieved by recirculating the oil and KPEG via a pump and high shear mixer, through a shell and tube heat exchanger. The heat transfer fluid on the shell side of the heat exchanger was heated using a boiler or cooled through a series of radiator type air coolers. The PCDD- and PCDF-contaminated oil was treated in five batches, each consisting of 1400 to 2000 gallons, requiring 600 gallons of KPEG reagent per batch. The mixture was heated to 150°C and allowed to react for one and one half hours before cooling. The treated oil was pumped out of the reactor and into a holding tank to confirm by subsequent analysis that PCDDs and PCDFs in the oil had been destroyed below detection limits.

The data from the sampling and analysis of each tank revealed that all PCDDs and PCDFs were destroyed to below the 1 ppb detection limit. The treatment cost was only 10% of the projected incineration cost.

In August 1986 the equipment was transported to Kent, Washington at the request of U.S. EPA Region 10 and was used successfully to treat approximately 8000 gallons of 2,3,7,8,-TCDD-contaminated liquid waste discovered on an industrial hazardous waste disposal site.

Currently, a new, improved 1 to 2-cubic yard reactor, designed to treat both liquids and solids, is being constructed. In early 1987, field verification studies will be conducted with this new KPEG reactor on four selected PCDD/PCDF- and PCB-contaminated sites. In 1987, it is expected that the KPEG process can be demonstrated to be cost-effective when used at wood preserving and Superfund sites to

TABLE 2. LABORATORY-SCALE TREATMENT OF OIL

Contaminants CDD/CDF	Concentration in Untreated Oil (ppb)	Concentration in Treated Residue (ppb)		*MDC
		70°C, 15 min.	100°C, 30 min.	
TCDD (2,3,7,8-)	28.2	-	-	0.65
TCDD (total)	422	-	-	0.37
PeCDD	822	-	-	0.71
HxCDD	2982	-	-	2.13
TCDF (2,3,7,8-)	23.1	12.1	-	0.28
TCDF (total)	147	33.3	-	0.35
PeCDF	504	-	-	0.36
HxCDF	3918	4.91	-	0.76
HpCDF	5404	5.84	-	1.06
OCDF	6230	-	-	2.62

*Minimum detectable concentration in parts per billion.

destroy toxic halogenated pollutants in liquids, sediments, sludges and soils.

ACKNOWLEDGEMENTS

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SUPERCRITICAL SOLVENT EXTRACTION

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ABSTRACT

Supercritical fluids are compressed gases at a temperature just above the vapor-liquid critical point, and have unique physical properties that can be used to develop novel separation schemes. There have already been numerous successful applications in a wide variety of areas ranging from the food industry (decaffeination of coffee), pharmaceuticals, and even energy (tertiary oil recovery). Significant opportunities exist to apply the same type of technology to problems in environmental control.

This paper first discusses the technical advantages of supercritical fluid extraction and reviews the phase equilibrium methods for separation process design. It presents new results demonstrating the concept of "tailoring" solvents for specific separation applications, primarily by using mixed solvents or entrainers. These theoretical results have been applied to design detoxification plants and determine the technical and economic feasibility of this new processing method for the rapid and safe removal of contaminants from waste sites. Specifically, mobile units are proposed for on-site removal of organic contaminants from soil and regeneration of granular activated carbon used for wastewater cleanup. Such an application of supercritical fluid technology would eliminate the need for transportation and burial, at costs significantly less than that for traditional methods.

INTRODUCTION

Supercritical fluids (SCF's) are the medium for an exciting new separation technology which has the potential to provide a much safer and less expensive alternative for the detoxification of materials at waste sites and the delisting of industrial adsorbants. In recent years there have been a wide variety of successful new applications of SCF technology which demonstrate the technical feasibility as well as the cost-effectiveness of such processes. In this paper we discuss the theoretical basis of SCF processing and report on design and economic studies made at the University of Illinois aimed at the development of mobile units for waste treatment using SCF separations, in a manner to optimize safety, economics, and public acceptability.

A SCF is a fluid that has been heated and compressed beyond its critical temperature and pressure, existing as a single phase with some unique properties. It is quite dense, almost as dense as a liquid, which gives a large capacity for solutes; it has a high molecular diffusivity and low viscosity, which make it an ideal medium for efficient mass transfer; and finally it has and unusually high compressibility, which permits large density changes with very small pressure changes, thus yielding extraordinary selectivity characteristics.

The solubility of heavy organic solutes in SCF's is frequently many orders of magnitude greater than the solubility in an ideal gas. The ratio of these two solubilities is defined as the enhancement factor and values of 10^6-10^9 are quite common. In addition, we have found that a one phase mixture of a pure SCF and a properly-chosen chemical "entrainer" greatly increases the solubility of solid solutes and/or enhances the separation of two solutes. An "entrainer" is a small percentage (1-5%) of an additional solvent added to the SCF, such as acetone, alcohol, or water added to CO_2. This increase in solubility and separation is due to specific chemical interactions between the entrainer and the solute (e.g. Lewis acid/base interaction or hydrogen bonding). As an example of the effect that is possible, the increase in selectivity of the removal of acridine from an acridine/anthracene mixture when 1% entrainer is added to supercritical CO_2 is shown in Figure 1.

Different entrainers in different supercritical solvents will exhibit varying degrees of solubility and separation ability. A careful choice of the solvent and entrainer permits the exploitation of the chemical interactions with the solutes to be separated to create an optimum solvent mixture or "tailor" a solvent for a process. For example, the removal of trichlorophenol from contaiminated soil might be greatly increased by the addition of a small amount of amine as an entrainer. The specific chemical interaction between the acidic trichlorophenol and basic amine is likely to greatly increase the solubility. Since the equilibrium or maximum concentration of the solute in the SCF will ultimately determine the economic feasibility of SC extraction processes we recognize the importance of tuning solvent properties and compositions to maximize solubilities.

SCF technology has been widely used in many fields. In the oil industry "miscible flooding" with supercritical CO_2 has long been a highly successful technique in tertiary oil recovery. Also the Kerr-McGee prizewinning ROSE process uses supercritical pentane to permit the processing of heavier and dirtier crudestocks. In the food business supercritical CO_2 has been used for a variety of processes, including coffee decaffeination, flavor recovery, removal of cholesterol from eggs, defatting of foods, and others. There are many other applications now in practice, such as the extraction of thermally labile materials from natural products, separation of ethanol from fermentation beers, coal desulfurization and liquefaction, analytical techniques such as SCF chromatography, and more. Thus there exists copious proof of the technical feasibility and economic advantages of SCF processing.

Many of the above applications were originally developed empirically, and were limited due to the paucity of experimental data and scientific understanding of the SCF state that existed a few years ago. However recently a number of studies have been carried out which have given us not only a better physical understanding of the SCF state, but the data to develop valid and reliable mathematical models from which one may do economic feasibility studies as well as designs and scaleups [1-10]. In the work reported here we have relied heavily upon these recent research results, and they were essential to the design process.

There are two major ways in which waste materials are detoxified by SCF extraction. The first is the direct contact, or single step method, in which contaminated material, solid or liquid, is contacted directly with the SCF, which extracts the toxic substances in highly concentrated form for subsequent treatment. This method is generally used with solids and with liquid streams with relatively high contaminant concentrations. For more dilute liquid streams, a two-step method is generally superior. In this the contaminant is removed at ambient pressure and temperature by an adsorbant, for example granular activated carbon (GAC), and the adsorbant is subsequently regenerated by SCF extraction. Studies [11,12] have demonstrated such regeneration to be far superior to conventional thermal regeneration.

The types of environmental problems that seem best solved by SCF technology involve the removal of organics from the soils and sludges found in the 546 National Priorities List waste sites, the detoxification of leachates and groundwaters, plus the regeneration of the GAC used in thousands of industrial pollution control operations. In the past much material has been disposed of by burial, preceded by transportation to a chosen site. Burial will not be a viable alternative in the future, and the transportation itself constitutes a hazard. We and others have designed and shown economic feasibility for stationary SCF toxic waste removal plants, but these do not address both parts of the problem. Thus, we have developed designs and economic analyses for mobile SCF separation units, capable of transportation by highway trailer to waste sites for rapid setup and safe and economical operation on site.

CURRENT TECHNOLOGY

The methods in current use for hazardous waste treatment--particularly for the National Priority List Sites --represent an immediate response to very recently defined problems, but not viable long-range solutions. Up to the present there has been much emphasis on hazard containment and volume reduction, including the transportation of abandoned wastes to approved containment sites. Such procedures, however, are not long-term solutions; not only does this in no way lessen the total amount of material which must be detoxified, but substantial extra hazard, and public-perception of hazard, is introduced by the transportation process. The current direction of research therefore must be containment and on-site treatment, developing methods that can be applied economically to a variety of wastes and which produce treated materials suitable for reuse in industry or for return to the environment.

One of the methods which has been applied to detoxification of contaminated solids is incineration. This technology has been scaled for relatively mobile operation (6-8 semitrailers and several weeks for setup are required), and it does produce residues which can be buried on-site. The greatest limitation, however, is the cost, which has been variously estimated at $500-1000/yd^3.

The cost of incineration of GAC is comparable. Thermal regeneration permits reuse of GAC, but is expensive itself, and involves a substantial loss of capacity on each cycle. Thus the treatment of groundwaters and leachates with GAC is expensive by current technology. Various reports of GAC costs run from $0.35-1.50/lb.

There also exists a class of problems involving sludges, with relatively high concentrations of metals and organic materials. The best disposal method seems to be solidification for burial. Vendor and literature information compiled recently by the the EPA [13] indicates that alcohols, aldehydes, ketones, chlorinated hydrocarbons, organic acids, acid chlorides, phenols and other soluble organics tend to increase set times for some mixes, and cause consistently reduced durability in the solidified product. Extraction of the organic components cited is listed in the EPA report as a removal method which also has the advantages of volume reduction and conversion to nonhazardous material.

Thus current methods are improving and can accomplish detoxification of most types of waste, and mobile scale design and testing is in progress for some applications to allow on-site processing. However, even where the technology is adequate, the costs for the large-scale operations needed to impact even a portion of the sites on the National Priorities List alone is prohibitive.

RESULTS OF ECONOMIC FEASIBILITY STUDIES

The scope of these investigations encompasses the design and evaluation of mobile SCF units for the treatment of contaminated soils, organic removal from sludges, and the regeneration of spent GAC. Common features of the designs include modularization for ease of transportation, and include the production of a concentrated toxin discharge stream for chemical detoxification (such as by dehydrohalogenation). Each system consists of two essentially independent segments: a continuous SCF flow loop to control fluid density by step changes in pressure, for continuous removal of extracted organics, and a semi-batch or continuous contactor.

In the design and cost estimations presented here, we have drawn on the available thermodynamic data and mathematical models, as well as on the very limited rate information available, and where uncertainty existed, made rather conservative contingency assumptions. Thus we consider that the unit costs for processing put forth here may have an uncertainty as large as a factor of two. Nonetheless, the SCF technology appears to be so economically attractive that even a doubling of the estimated costs would represent very substantial savings over current technology.

Soil Systems

Soil detoxification is the most complicated of the three types of waste treatment problems studied. It may require site excavation to 10 feet or more to achieve complete removal of contaminants; pretreatment is required to screen large rocks and grind wood; and varying moisture levels necessitate process flexibility. Each factor leads to more peripheral equipment, which exacerbates both the processing and mobility problems.

Constraints for this design include the limitation to a total of six semi-trailers, including pretreatment, laboratory, and control room facilities. Other design bases include semi-batch operation of the contactor units and a set ratio of 8 lbs. SCF/lb. soil treated in the detoxification cycle (for pure CO_2 solvent). The latter condition (possibly too conservative) is based on the preliminary results reported by Knopf et al. at Louisiana State University [14]. Under these conditions highway weight limits result in treatment capacity of 50 yds^3/day (2.1 yds^3/hr.). If necessary permits could be obtained (as seems likely) for 20% overweight on one trailer, the capacity could be expanded by 78% (3.7 yds^3/hr, or 89 yds^3/day). The design results are summarized in Table I and Figure 2.

Sludge Systems

Organics removal from high-metal sludges has the potential to be a vastly simpler process if the sludge is pumpable, so that completely continuous countercurrent processing can be used. Data are limited at this point, but it appears that capital costs might be comparable to those for SCF soil processing, and operating costs could be a bit more favorable in a continuous process.

GAC Systems

The handling of leachates and groundwaters is really just an application of the GAC technology. These generally represent a situation where the contaminant is dilute, and a two-step separation is appropriate. Thus one would envision an adsorption on GAC, followed by SCF regeneration.

The regeneration of spent GAC is essentially just a simplified version of the soil treatment process because any screening or grinding pretreatment operations are unnecessary. The solids are more homogenous so less variations in processing are required. They are also more flowable, which facilitates easier semi-batch or even continuous operation of the separator modules. Finally the volume to be treated is normally much less. We have developed a design for a mobile unit carried on just two trailers with a regeration capacity of 500 lbs./hr. (dry basis), and we have used the same flow ratio that we have used previously in stationary plants, 20 lbs. SCF/lb.dry GAC. Capital and operating costs have been scaled from the designs for soil detoxification, and the economic summary is given in Table II.

To calculate return on investment we have made the rather conservative assumption that the total cost of thermal regeneration and make-up GAC to offset capacity reduction are at least 35¢/lb. The minimum net gain is then at least 20¢/lb, since GAC regeneration by SCF processing is estimated at 15¢/lb.

CONCLUSIONS

From these economic studies, it is easily concluded that supercritical extraction offers an attractive alternative to several current hazardous materials treatment methods. However, before construction of a full-scale operational mobile detoxification unit based on SCF technology, an intermediate bench scale or pilot unit should be constructed and operated on a batch or semi-batch basis.

The following points should be taken into consideration. The results of the above research should be incorporated into any design and the best system to use for the initial study would be a unit for regeneration of GAC. The unit should be sized so that only one scale-up step is needed, which means a bench-scale unit processing 50-100 lbs/day of GAC (dry basis). The unit should be operated over a wide range of operating conditions and the possibility of a continuous contactor for flowable GAC in contact with a supercritical fluid should be investigated.

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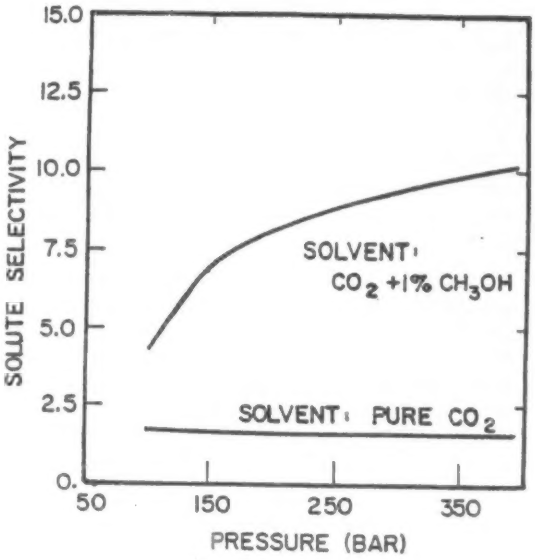

Fig. 1 Entrainer effect on selectivity: The supercritical fluid extraction of acridine from phenanthiene.

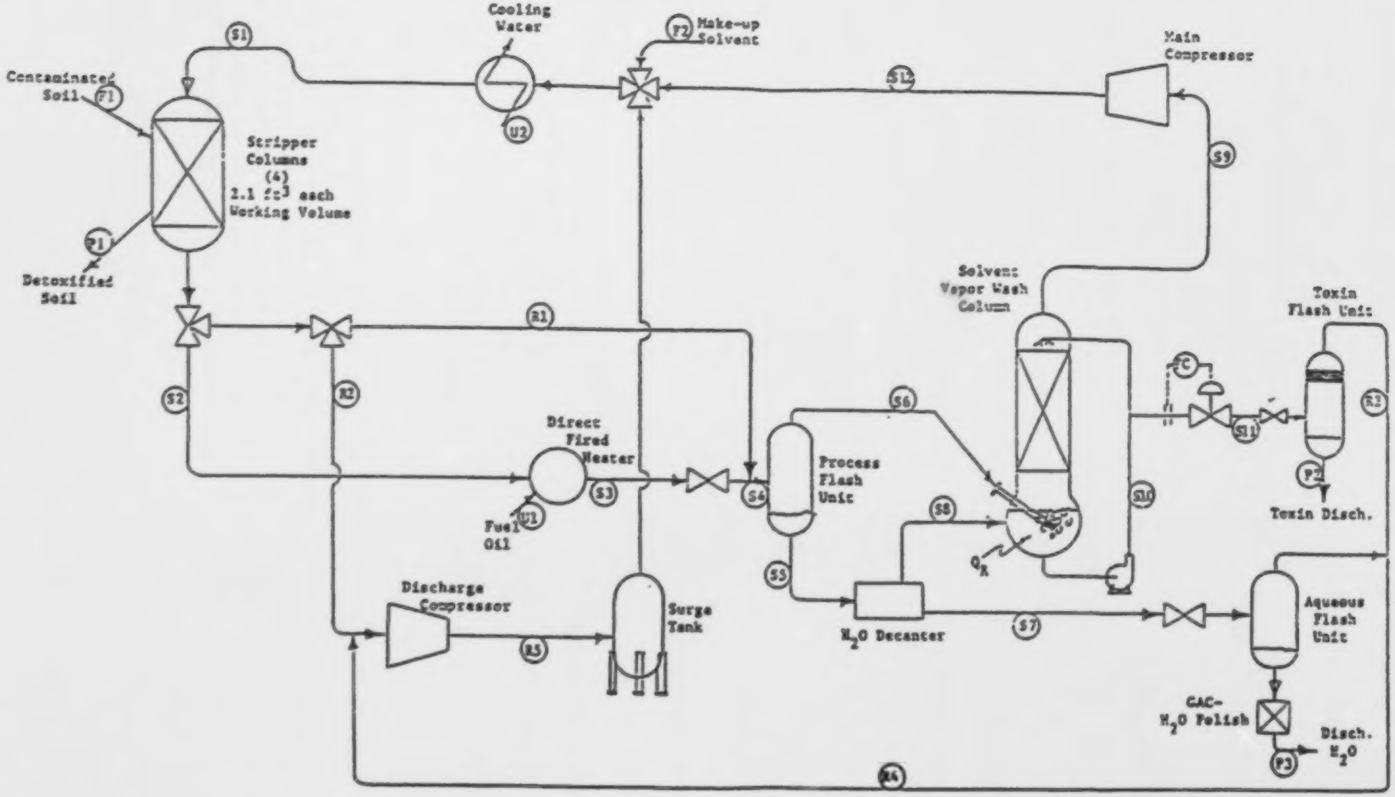
Contaminated Soil
F1
S1
Cooling Water
U2
P2 Make-up Solvent
S12
Main Compressor
S9
Stripper Columns (4) 2.1 ft^3 each Working Volume
P1
Detoxified Soil
R1
S2
R2
Direct Fired Heater
Fuel Oil
U1
S3
S4
Process Flash Unit
S6
S5
S8
H_2O Decanter
S7
Solvent Vapor Wash Column
Q_R
S10
FC
S11
Toxin Flash Unit
R3
P2
Toxin Disch.
Aqueous Flash Unit
GAC-H_2O Polish
P3
Disch. H_2O
Discharge Compressor
R5
Surge Tank
R4

Figure 2. Flowsheet for mobile detoxification unit for supercritical fluid extraction of contaminated soil.

TABLE I
SCF EXTRACTION OF CONTAMINATED SOIL

Design Basis: 2.1 yd^3/hr., 250 days/yr.

CAPITAL COSTS	MM\$
EQUIPMENT	1.45
ENGINEERING AND SUPERVISION	0.15
CONSTRUCTION	0.15
CONTINGENCY	0.20
WORKING CAPITAL	0.25
TOTAL CAPITAL INVESTMENT	2.20
OPERATING COSTS	M\$/YR
DIRECT COSTS:	
Solvent	10.8
Labor	225.0
Direct Supervision	30.0
Utilities	170.4
Maintenance and Repairs	110.0
Operating Supplies	11.0
Laboratory Costs	30.0
	587.2
FIXED CHARGES:	
Depreciation	145.0
Taxes and Insurance	39.0
Plant Overhead	73.0
Administrative Costs	20.0
Financing	220.0
	497.0
CONTINGENCY FOR TRANSPORTATION:	150.0
TOTAL PRODUCT COST:	1234.2

UNIT COST = \$98.74/YD^3

COST FOR MOBILE INCINERATOR	\$500/yd^3
ANNUAL PRETAX PROFIT	\$5.02MM
RETURN ON INVESTMENT	228%
PAYOUT TIME	5.3 MONTHS

TABLE II
SCF REGENERATION OF CONTAMINATED GAC

Design Basis: 500 lbs/hr GAC, dry basis
10,000 lbs/hr CO_2 recirculation
250 days/year operation

CAPITAL COSTS:	M\$
Vessels (4 @ 16 ft^3)	216.0
Main SCF Loop	213.4
Recovery System	65.4
Cooling Tower	6.0
Material Handling, Conveyors	15.8
Process Trailer	15.0
Analytical/Office Trailer	100.0
Direct Capital Investment	634.6
Engineering and Supervision	50.0
Construction Expense	50.0
Contingency	50.0
FIXED CAPITAL INVESTMENT	784.6
Working Capital	100.0
TOTAL CAPITAL INVESTMENT	\$884.6
OPERATING COSTS:	M\$
DIRECT COSTS:	
Makeup CO_2	2.5
Labor (4 @ 25,000)	100.0
Supervision (½ @ 30,000)	15.0
Utilities	39.5
Maintenance and Repairs	44.2
Operating Supplies	4.4
Laboratory Costs	30.0
	235.6
FIXED CHARGES:	
Depreciation	63.5
Taxes and Insurance	15.7
Plant Overhead	31.8
Administrative	10.0
Financing	88.5
TOTAL PRODUCT COST	445.1

UNIT COST: 14.8¢/lb dry GAC

CURRENT TECHNOLOGY: Thermal regeneration costs at a minimum 35¢/lb including replacement of spent GAC but not including disposal cost for unusable GAC. Incineration/replacement as an alternative may range as high as \$1.50/lb. Thus we use minimum "profit" of 20¢/lb.

RETURN ON INVESTMENT >68%
PAYOUT TIME <18 MONTHS

SUPERCRITICAL FLUID EXTRACTION AND CATALYTIC OXIDATION OF TOXIC ORGANICS FROM SOILS

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ABSTRACT

Supercritical fluid (SCF) extraction is a promising new technique for the cleanup of soils, sediments, and sludges that are contaminated with hazardous wastes. In this investigation, supercritical carbon dioxide (SC-CO_2) has been used to extract PCBs, DDT, and toxaphene from contaminated topsoils and subsoils. An attractive feature of this process is that the CO_2, being virtually inert, leaves no solvent residue on the processed soil.

In our initial extraction studies, supercritical CO_2 at 100 atm and 40°C was continuously passed through a fixed bed of 10 g of soil. Approximately 70% of the DDT and 75% of the toxaphene could be leached from a topsoil (12.6% organic matter) contaminated with 1000 ppm DDT and 400 ppm toxaphene in under ten minutes using SC-CO_2 at a rate of 0.7 g/s. The extraction of contaminated (with 1000 ppm Aroclor 1254) subsoil (0.74% organic matter) proved to be even more promising, because more than 90% of the PCBs could be extracted in under one minute at the same CO_2 rate.

Recently SC-CO_2 with a single entrainer[*], either methanol or toluene, was compared to pure CO_2; comparison was made on the basis of extraction rate and the removal efficiency for DDT or PCBs from contaminated topsoils. The supercritical mixtures at 100 atm and 40°C were continuously passed through a fixed bed of 10 g of soil. The most effective solvent system, SC-CO_2 with 5 wt% methanol at a flowrate of 0.7 g/s, was able to leach 95% of the DDT from the soil in under 5 minutes, as compared to either pure CO_2 or CO_2 with 5 wt% toluene at the same conditions, which resulted in only 70% extraction in 10 minutes. This same extraction mixture (SC-CO_2 with 5 wt% methanol) was also applied to a highly contaminated spill site topsoil containing ca. 3500 ppm Aroclor 1260 and 2100 ppm Aroclor 1242. Over 98% extraction of the contaminants was realized in 10 minutes.

With the demonstrated ability to extract contaminants from soils using supercritical CO_2 with an entrainer, a logical further treatment would be the destruction of the wastes while they are in the supercritical phase. An evaluation of catalysts for the low temperature (below 350°C) oxidation of polycyclic aromatic hydrocarbons and chlorinated hydrocarbon wastes in the SCF phase will be presented.

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[*] An entrainer is a volatile organic compound which, when added in low levels to supercritical CO_2, dramatically increases the solubilities of certain nonvolatile organics in the SCF.

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INTRODUCTION

Supercritical fluid (SCF) extraction has received much attention as a technique for separating relatively nonvolatile materials (Paulaitis et al., 1982). Typically in SCF extraction a solvent gas such as carbon dioxide, at high pressure and moderate temperature, is contacted with a solid or liquid phase. Slight changes in the system temperature or pressure can cause large changes in the solvent density and consequently in its ability to solubilize relatively nonvolatile components. For example, at 200 atm and 35°C the density of CO_2 approaches 0.8 g/cc and at these conditions a solute such as naphthalene would have a solubility some 10,000 times that predicted if CO_2 behaved as an ideal gas. By taking advantage of these facts a process can be envisioned whereby manipulation of the system pressure effects extraction of a nonvolatile material. A pressure letdown, to a pressure below the system critical conditions, can cause near complete precipitation of the relatively nonvolatile material from the solvent. In addition to the liquid-like densities of a typical SCF, viscosities and molecular diffusivities of SCFs are intermediate to typical liquid and gas values for these properties. For these reasons the extraction efficiencies of SCFs are usually higher than those of liquids.

The many advantageous properties of SCFs have opened up new technologies in environmental control; the subject has been recently reviewed by Groves, Brady and Knopf (1985). Successful efforts have included the use of SCFs in: the regeneration of adsorbents contaminated with volatile organics using pure SC-CO_2 (Eppig et al., 1981); oxidation of organic contaminants in waste streams using SC-water (Modell, 1982); liquid-liquid extraction of waste streams again using pure CO_2 as the extraction medium (Ringhand and Kopfler, 1983); the extraction/reaction comprising the generation of low sulfur chars from coals utilizing either SC-toluene or SC-alcohols (Vasilakos et al., 1985); and finally the regeneration with SC-CO_2 of activated carbon used in the cleanup of liquid waste streams (de Filippi et al., 1980a). The regeneration of activated carbon was not universally practical, because the buildup of irreversibly bound organics frustrated some applications.

We are currently examining the capabilities of supercritical fluids to extract toxic chemicals such as DDT and PCBs from soils, thereby providing a tool for cleaning up hazardous waste sites. Such removal offers the obvious advantage of the creation of a much smaller volume if further treatment such as combustion, biological degradation or other disposal method is desired.

In conventional extraction technology the pressure would be reduced subsequent to extraction, precipitating a solid or liquid phase rich in organic contaminants from the CO_2. In order to recycle the CO_2, the contaminant level in the CO_2 must often be further reduced by distillation (deFilippi et al, 1980b). In addition, since the pressure of the CO_2 has been substantially lowered, recompression is necessary.

In conjunction with our work with SC-CO_2 plus entrainers, we are investigating an alternative to the above separation scheme. We are attempting to totally oxidize the extracted organic contaminants by passing the high pressure mixture plus air over total oxidation catalysts such as CuO. Temperatures necessary for total oxidation should be in the 420-600 K range, this being characteristic of free-radical assisted autoxidation processes (Schuit and Gates, 1980). After drying to remove the water formed in the reactions, and neutralization, both of which can be accomplished at high pressure, the CO_2 can be recycled with small recompression costs.

In order to explain the extraction process, the thermodynamics involved, and oxidation catalysis in a supercritical fluid medium, this paper is divided into two sections. The first discusses background, including early SCF extraction results and the phase equilibria expected for the ternary system of CO_2-methanol-DDT (here methanol is an entrainer), and briefly introduces both reactions in SCFs and catalytic autoxidation of priority pollutants. The second section presents recent data on the effectiveness of CO_2 with entrainers for the extraction of DDT and PCBs from topsoils of high organic content. Some preliminary data showing the solid-catalyzed partial oxidation of a pollutant (toluene) in a SCF are also presented.

PAST RESULTS

In previous work (Brady et al., 1987) we investigated the use of pure SC-CO_2 to extract PCB's, DDT and toxaphene from a contaminated topsoil (12.6% organic matter) and subsoil (0.74% organic matter). Experiments with SC-CO_2 continuously flowing through a fixed bed of 10 grams of contaminated soils showed that over 90% of the PCBs (original contamination level 1000 ppm) could be extracted from the subsoil in under one minute using a CO_2 flowrate of 0.7 g/s. However, only 70% of the DDT and 75% of the toxaphene could be leached from the topsoil contaminated with 1000 ppm DDT and 400 ppm toxaphene in 10 minutes at the same CO_2 rate. These results are not unexpected in that pure SC-CO_2, being a relatively nonpolar solvent, would show only non-specific van der Waals interactions with adsorbed compounds that may be strongly bound to polar sites on the topsoil. The presence of these sites is consistent with the high organic content of the topsoil. Mixed solvents, for example CO_2 and a few wt% of a polar entrainer, could result in specific chemical attraction of adsorbate and extraction medium, and thus enhance contaminant extraction from solids containing polar adsorption sites, such as activated carbon or topsoils of high organic content.

PHASE DIAGRAMS

The "entrainer" solvents used in this work to date are toluene and methanol. By using the Peng-Robinson cubic equation of state (Peng and Robinson, 1976), the triangular phase diagram for the ternary system CO_2-DDT-methanol at 40°C, 100 atm can be constructed as shown in Figure 1.

It is assumed the solubility of the solvent (CO_2 with methanol) in solid DDT (component 2) is negligible. The solid phase is considered pure DDT, and its fugacity f_2^{os} in phase equilibria calculations was evaluated from

$$\ln \frac{f_2^{os}}{f_2^{ol}} = \frac{\Delta H^f}{R}\left(\frac{1}{T_{m_2}} - \frac{1}{T}\right) - \int_0^P \frac{V_2^{ol} - V_2^{os}}{RT}\, dP \quad , \qquad (1)$$

assuming the Peng-Robinson equation is valid for calculating the fugacity of the pure subcooled liquid (f_2^{ol}). The critical points are calculated according to the algorithm proposed by Heideman and Khalil (1980).

At 40°C and 100 atm, the addition of a small amount of toluene or methanol to CO_2 increases the DDT solubility. The solubility of DDT in a mixed solvent of 95 wt% CO_2 and 5 wt% toluene is estimated as 2.5×10^{-3} (~3.6 times the value in pure CO_2). If toluene is replaced by methanol the estimated DDT solubility from Figure 1 is 0.01 (~14 times that in pure CO_2). Therefore a mixed solvent with 95 wt% CO_2 and 5 wt% methanol should be more effective in extracting DDT from soil than a mixed solvent with 95 wt% CO_2 and 5 wt% toluene, although the latter is still a more effective solvent than pure CO_2. The approximate supercritical phase compositions for the ternary system at the operating conditions are summarized in Table I. The interaction parameter k_{ij} (k_{ij} = 0.07) was empirically determined by regressing VLE data for the binary system of CO_2 plus methanol (Semenova et al., 1979). The phases present ("conditions") are denoted by either SFE (solid and SCF at equilibrium) or SLVE (solid-liquid-vapor phases at equilibrium).

Table I. Compositions of Supercritical Fluid Phases for CO_2-Entrainer-DDT-Systems

System	k_{ij}	Mol Fraction (40°C, 100 atm)		Condition
$CO_2(1)$ + DDT(2)	0.07	$y_2 = 0.7 \times 10^{-3}$		SFE
DDT(2) + Methanol	0	$y_2 = 0.3 \times 10^{-3}$		SFE
CO_2 + DDT + Methanol		$x_2 = 0.055$	$x_3 = 0.132$	SLVE
		$y_2 = 0.014$	$y_3 = 0.079$	
		$x_2 = 0.032$	$x_3 = 0.115$	critical pt

REACTIONS IN SUPERCRITICAL SOLVENTS

Supercritical fluids have potential advantages as solvents in coal liquefaction, high temperature thermal condensations and alkylations, catalyzed hydrocarbon isomerizations, and oxidation reactions. The application of SCF solvents improves the final product distributions of these reactions, sometimes by diminishing heat and mass transport limitations, and sometimes by allowing separation of desired products prior to further reaction in a solid or liquid phase. Currently, the most promising application of SCF as reaction media is coal liquefaction/extraction, where the condensed extract is a fuel or chemical feedstock comparable to hydrogen-intensive processes. These findings have prompted a growing interest in reactions using supercritical fluid media, the subject has been recently reviewed (Subramaniam and McHugh, 1986).

The utility of SCF as reaction media, apart from their utility in coal processing, is documented. SCF have proven feasible as reaction media for high temperature deep oxidations (Modell, 1982), where SC water homogenizes heavy organic-air-salt mixtures and thereby enhances combustion efficiencies.

SCF have also proven feasible as reaction media for hydrocarbon isomerization processes, either with a homogeneous or heterogeneous catalyst (Kramer and Leder, 1975, Tiltscher et al., 1981). The details of the isomerization processes are sketchy but interesting. In the homogeneous process, the SC paraffin reactant solubilizes not only the most efficient catalyst, $AlBr_3$, but also H_2, which controls the selectivity of this reaction by suppressing cracking rates. Isomerization-to-cracking ratios of better than 50 were obtained at optimum reaction conditions.

Finally, Metzger et al. (1983) have found that many compounds containing carbonyls or double bonds will undergo condensation and alkylation reactions at temperatures not much above their critical temperatures, in the 300-600K range. At these conditions they prepared, for example, the cyclohexane addition products to acrylonitrile, heptene-1, and methyl acrylate in high yields. The intermediates in these reactions were remarkable stable with respect to polymerization.

In summary, it has been observed that SCF provide favorable reaction media in the following cases:

(1) Where homogenization of the reaction mixture removes diffusion limitations for a key reactant, catalyst, or promoter;

(2) Where the SCF separate unstable products of reaction from a solid or liquid phase.

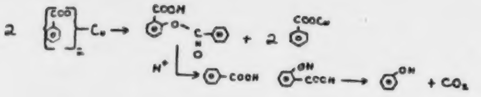
(3) Where the SCF play a direct role in reaction, say, in the stabilization of free radicals or other intermediates, or assisting in the transfer of hydrogen.

(4) Where the SCF aid in the solubilization of reaction products that could result in catalyst deactivation.

TOTAL CATALYTIC OXIDATION OF PRIORITY POLLUTANTS

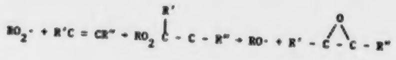
The chemical behavior with respect to catalytic total oxidation of the many compounds listed as priority pollutants (U.S. EPA, 1980b; Robertson et al., 1980) is so diverse that not all compound classes could be studied. This is true even if we restrict ourselves to single model compounds or well-characterized mixtures of homologous compounds. Our attention has been focused on three classes of difficult-to-oxidize compounds: (1) Single-ring aromatics with deactivating side groups, such as chlorobenzenes, chlorobenzidines, and nitrophenols; (2) Fused-ring polycyclic aromatic hydrocarbons (PAHs) such as anthracene and benzanthrene; (3) Chlorinated biphenyls and naphthenic compounds such as DDT, PCBs, and dieldrin. Our catalytic oxidation work is not performed independently of the entrainer studies; feeds to be oxidized include the entrainer, which in some cases will be oxidized as well. Entrainer oxidation is often desirable, since in free radical processes small molecules that can form radicals easily (acetone, for example) help initiate the more difficult free radical oxidations of the refractory compounds. Such oxidizable initiators are known as co-oxidants and represent a more economical solution to the initiation problem than do such common initiators as peroxides.

We have examined total oxidation by free-radical-assisted redox processes, which are well known for the partial oxidations of alkylaromatic and naphthenic hydrocarbons in aqueous or organic solutions; the reaction mechanisms and applicable catalysts are exhaustively surveyed by Kaeding et al. (1970), Sheldon and Kochi (1974), Schuit and Gates (1980), and Parshall (1980). The catalysts are organometallic redox couples containing, for example, Co^{2+}/Co^{3+}. Peroxides and hydroperoxides are the primary products, which decompose to more stable products at temperatures above about 80-100°C. Typical pathways for a typical reaction, the oxidation of toluene to benzaldehyde/benzoic acid, are given in Fig. 2. In the presence of acids, condensation takes place concurrently with oxidation, resulting in the production of phenols and acetates. A typical pathway for toluene oxidation is given below:



The processes and catalysts common to solution can be adapted to a dense gas (supercritical) phase and certain solid heterogeneous catalysts. We have demonstrated this in a recently completed study of the oxidation of toluene to benzaldehyde with feeds composed mostly of supercritical CO_2 and some air (Dooley and Knopf, 1986). Not all redox-containing catalysts are effective; in fact, in catalytic reaction experiments employing a series of Co and Co-Mo oxides supported on Al_2O_3, only one catalyst with a specific Co^{2+}/Co^{3+} initial ratio was both active for partial oxidation and inactive for the undesired condensation reactions to polycyclic products. For this work the temperatures were in the 180-220°C range and the catalysts were not modified with electron transfer promoters (as they are in solution) to enhance their activities.

At slightly higher temperatures and with the inclusion of electron transfer promoters in the solid catalyst, peroxides and hydrogen peroxides are more easily produced and then ruptured at the O-O bond. The rupture results in a net increase in the number of free radicals and therefore in a dramatic increase in oxidation rates. Schuit and Gates (1980) have shown that at these conditions the total concentration of peroxides and hydroperoxides is proportional to the exponential of the product of the rate of formation of all products times the reactor residence time. Therefore once initiated this process must result in complete oxidation of all oxidizable species present in the feed, if the amount of catalyst employed is large enough. One way in which olefinic, aromatic, and other double-bond containing molecules can be totally oxidized is through free-radical epoxidation on a surface or even by desorbed radicals in the fluid-phase (Haber, 1985):



$$RO_2\cdot + R'C = CR'' \rightarrow RO_2\overset{R'}{\overset{|}{C}} - C - R'' \rightarrow RO\cdot + R' - \overset{O}{C - C} - R''$$

The reason why total oxidation is not more prevalent in solution is that the reaction conditions are carefully chosen to inhibit this generally undesired reaction: the solutions are O_2 starved due to the low solubilities of low-pressure air in most organics, and the solutions often contain polar compounds (acetic acid, for example) which act as free radical traps. Both of these limits on total oxidation will be removed in the proposed process. The upper limit on free-radical-assisted total oxidation is about 300-350°C; above these temperatures the reverse rates of hydroperoxide formation reactions are large enough that oxidation must take place by other routes.

Simple oxides may not catalyze the total oxidation of refractory aromatic and naphthenic compounds. The ideal catalyst must be able to adsorb the hydrocarbon by electron transfer to or from a metal cation site, to insert electrophilic oxygen to form aldehydes or epoxides, and finally to decompose these to carbon oxides.

EXPERIMENTAL METHODS FOR SCF SOIL EXTRACTIONS

Two contaminated topsoils were obtained for our extraction experiments. The first topsoil was obtained from a DDT spill site near Lake Providence, Louisiana. The second topsoil was obtained from a PCB spill site. The soils were air-dried (35°C) and the initial DDT or PCB levels checked via EPA-approved test procedures (U.S. EPA, 1980; 1982).

A schematic diagram of the $SC-CO_2$ extraction apparatus is given in Figure 3. Liquid CO_2 at ambient temperature is fed to a diaphragm compressor and compressed to a pressure between 200 and 350 atm. The compressed CO_2 is stored in surge tanks to dampen any pressure fluctuations. From the surge tanks the CO_2 flows at ~0.7 g/s to a vertical tube fixed bed containing the contaminated soil; the pressure here is controlled to ±5 psi. Upstream of the vertical tube, approximately 5 wt% of either toluene or methanol are combined with the supercritical CO_2 by the use of a Ruska high-pressure metering pump. In the tube the fixed bed of contaminated soil is contacted by the mixed solvent. The extraction pressure is monitored by a Heise digital pressure gauge. Both the feed line and the fixed bed are immersed in a constant temperature bath maintained at 40 ± 1°C. Downstream of the bed two micrometering valves are used to control the solvent flow rate and reduce the pressure to atmospheric. The extract mixture is first passed through two dry ice/acetone cold traps to collect the precipitated contaminants, followed by an activated carbon trap, and finally by a dry test meter to totalize the solute-free CO_2. All wetted parts of the apparatus are stainless steel, teflon, or viton.

The residual concentration of DDT or PCBs in the soil is measured according to EPA-approved test procedures (U.S. EPA, 1980; 1982). Typically 5 g of soil are weighed to ± 0.01 g into cellulose extraction thimbles, which are placed in a Soxhlet apparatus and extracted for 8 hours with a 60/40 mixture of acetone/hexane. The acetone/hexane extracts are then washed with water to remove acetone, and the hexane portion is subjected to florisil cleanup and finally diluted with hexane as necessary for analysis by gas chromatography.

SCF EXTRACTION OF DDT CONTAMINANTED TOPSOIL - RESULTS AND DISCUSSION

The initial DDT level of the contaminated topsoil was 1271 mg/kg. Extractions of this test soil showed that approximately 60-70% of the DDT could be removed in approximately 10-20 minutes as shown in Figure 4. Longer-time extractions using pure SC-CO_2 did not show any improvement over this reduction. These data imply that a portion of the DDT is strongly bound to the soil and that SC-CO_2 at these conditions cannot extract this strongly-bound DDT.

Using the same extraction conditions as with pure SC-CO_2 (40°C, 100 atm, flow rate ~ 315 cm^3/s at 25°C, 1 atm), the two mixed solvent systems (CO_2-toluene and CO_2-methanol) were investigated. These data are plotted in Figure 4 along with the extraction data obtained using pure SC-CO_2 solvent. Little if any improvement in extraction efficiency is observed upon comparing the data for SC-CO_2 with 5 wt% toluene to that for pure SC-CO_2. A maximum of 60-70% of the DDT can be removed in 10-20 minutes with either solvent system. Extraction with SC-CO_2 and 5 wt% methanol, however, is more successful. Approximately 95% of the contaminants can be removed in 5 minutes or less (Figure 4). These results imply that for maximum extraction efficiency a mixed solvent system should be used, where the entrainer or co-solvent is tailored to the soil type and the solute being extracted.

To determine the rate-limiting-step of the extraction process, we also carried out extractions of DDT-contaminated topsoils at various SC-CO_2 flowrates, while maintaining the methanol entrainer composition at 5 wt%. These results are presented in Table II. The data indicate that the process is apparently not external-transfer limited (in the fluid phase).

Table II. Variation of Soil Concentration in the Extraction of DDT-Contaminated, Spill-Site Topsoil using SC-CO_2 with 5 wt% Methanol

Conditions: 40°C, 100 atm, 470 and 47 cm^3/sec

Extraction Time (min)	470 cm^3/sec @ 25°C, 1 atm	47 cm^3/sec @ 25°C, atm
0	1271	1271
1	221, 207*	—
1	222, 236	—
2	82, 105	—
2	95, 94	—
5	66, 58	60
5	58, 61	—
10	52, 37	—
10	59, 48	—
20	—	86
40	—	34
60	—	51
120	—	25

*Multiple entries in concentration column are replicate analyses.

SCF EXTRACTION OF PCB CONTAMINATED TOPSOIL - RESULTS AND DISCUSSION

To again demonstrate the effectiveness of SC-CO_2 with 5 wt% methanol, this solvent system was used to extract a spill site topsoil containing ca. 3,500 ppm Aroclor 1260 and 2,100 ppm Aroclor 1242. The results, plotted in Figure 5, show over 98% removal of the contaminant is possible within a 10 minute extraction period.

EXPERIMENTAL METHODS FOR SCF OXIDATION STUDIES

We are currently investigating the oxidation of toluene with redox catalysts, using the system shown in Fig. 6. CO_2 is compressed to slightly above critical conditions (T_c = 31°C and P_c = 72.8 atm), and at a flow rate of 1 g/s is mixed with toluene delivered by a metering pump and air from a cylinder. All flow rates are controlled by metering valves. The reaction mixture is ca. 1.5 wt% toluene, 1.5% oxygen, 5% N_2, and 92% CO_2, and is controlled at 30-300°C ±1°C by encasing the reactor (½" o.d. tube with a fritted disk) in an insulated heat source (4" o.d. heated alumnium block). For the initial experiments the pressure at the reactor was 80 atm although the reactor is capable of pressures in excess of 300 atm.

Before the reactor, the air/CO_2 ratio and toluene/CO_2 ratio are checked by on-line sample injection into a gas chromatograph with a thermal conductivity detector; after the reactor, product samples are injected into an on-line gas chromatograph interfaced to a mass spectrometer (Extrel Model ELQ 400) for detailed analysis. The products are then cooled by expansion through a heated micro-metering valve. The uncondensed CO_2 is passed through a totalizing meter.

It was possible to dissolve 1.5 wt% toluene and 6.5 wt% air in supercritical CO_2 at 80 atm and 293-493K. Using this mixture the toluene could be oxidized at low rates and conversions to benzaldehyde, benzyl alcohol, the cresol isomers, and a lesser amount of condensation products and carbon oxides. A 5% CoO/Al_2O_3 catalyst, calcined at 200°C in order to preclude oxidation to Co_3O_4 and the cobalt "aluminates", proved to be an active and selective (for partial oxidation) catalyst. Its turnover number for partial oxidation was about 10^{-5}/s at 473K.

SUMMARY

We have reported the use of SC-CO_2, with either toluene or methanol as an entrainer, for the extraction of DDT and PCBs from contaminated topsoils. The extraction efficiency was shown to be a strong function of the entrainer selected. A supercritical mixture of CO_2 plus 5 wt% toluene showed no improvement over CO_2 alone, with only ~ 75% removal of the DDT possible; the residual DDT was strongly adsorbed on the soil. However, near complete removal of DDT was possible using SC-CO_2 with 5 wt% methanol at 40°C and a flowrate of 0.7 g/s. The efficiency of the CO_2-methanol system remained unchanged with a large variation in flowrate, from 1 g/s to 0.1 g/s, demonstrating that no external transfer resistances are present at these conditions. Near complete removal of a mixture of Aroclor 1260 and Aroclor 1242 was also possible using SC-CO_2 with 5 wt% methanol at 40°C and a flowrate of 0.7 g/s. Once these contaminants have been dissolved in the SCF phase, partial oxidation is feasible if catalyzed by certain supported metal oxides. Further work on total oxidation by supported mixed-metal oxides is in progress.

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NOMENCLATURE

F = fluid phase

f = fugacity, atm

ΔH^f = heat of fusion, cal/mol

k = interaction parameter

L = liquid phase

P = pressure, atm

R = gas constant, 1.987 cal/mol-°K or 82.06 atm-cm^3/mol-°K or soil particle radius, cm

S = solid phase

T = temperature, °K

V = vapor phase or molar volume, cm^3/mol

SUBSCRIPTS

m = melting point

o = initial value

1 = supercritical solvent

2 = solute

SUPERSCRIPT

$o\ell$ = pure subcooled liquid

os = pure solid

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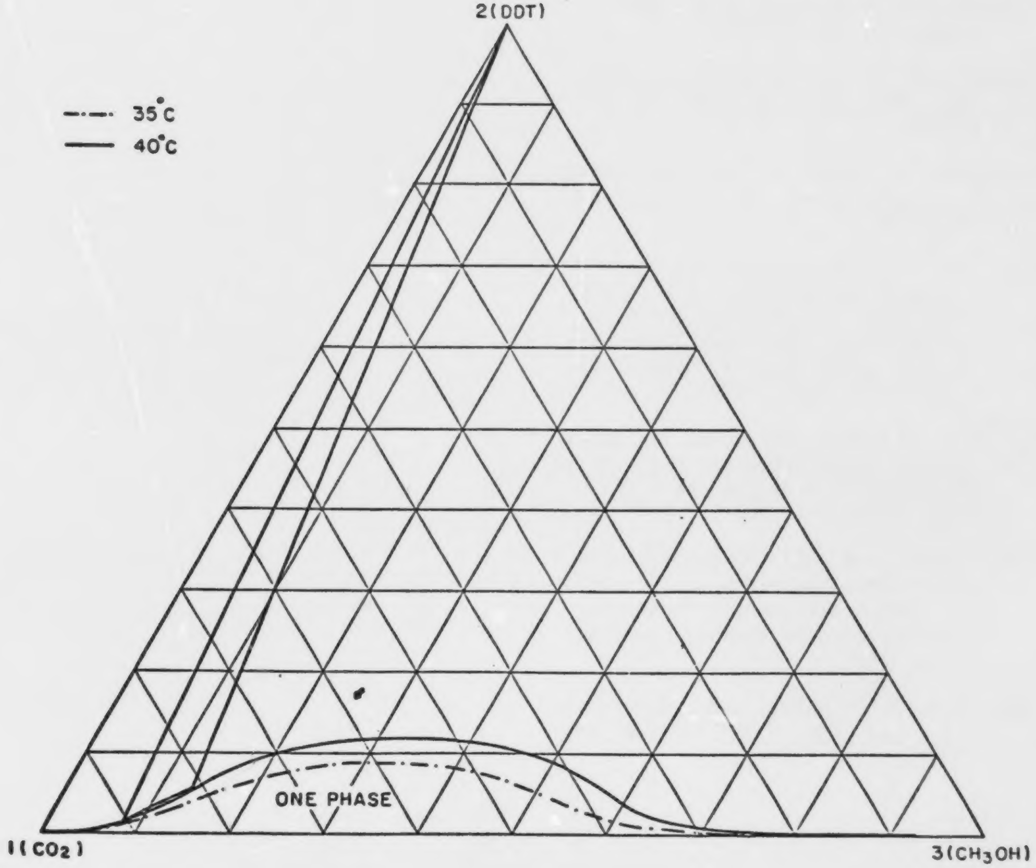
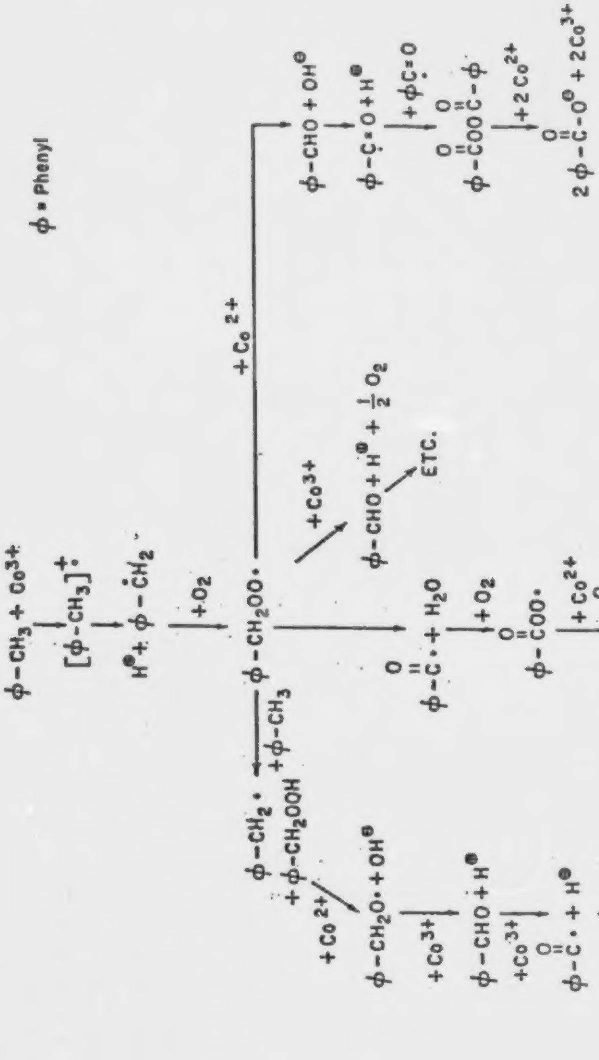


Figure 1. Phase behavior of the ternary system of CO_2-DDT-methanol at 35°C and 40°C, 100 atm.



φ = Phenyl
(Peroxybenzoate)
(Benzoate)
ETC.

Figure 2. Pathways for toluene oxidation.

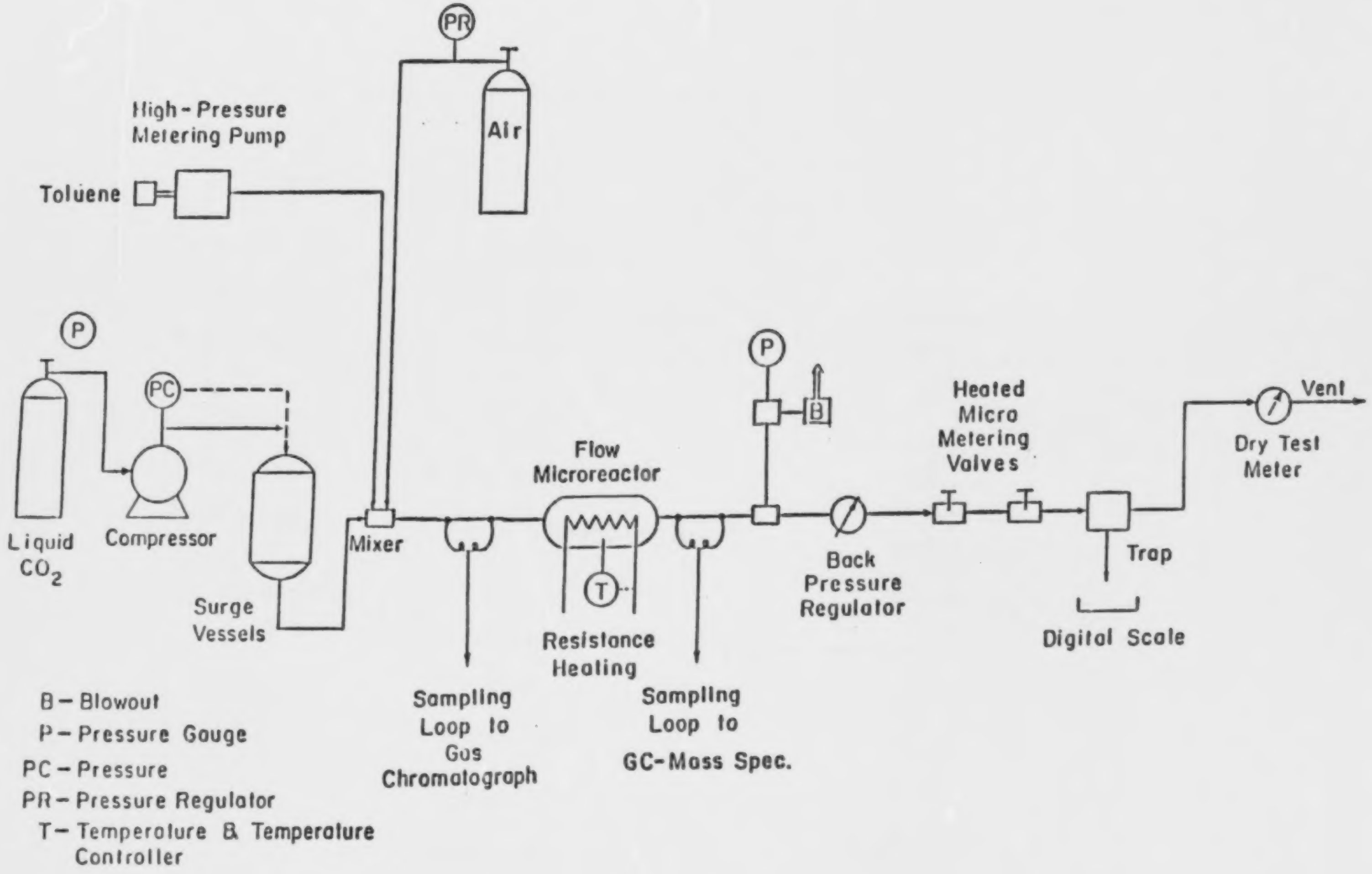

PR
High-Pressure Metering Pump
Toluene
Air
P
PC
Liquid CO2
Compressor
Surge Vessels
Mixer
Sampling Loop to Gas Chromatograph
Flow Microreactor
T
Resistance Heating
Sampling Loop to GC-Mass Spec.
P
B
Back Pressure Regulator
Heated Micro Metering Valves
Trap
Digital Scale
Vent
Dry Test Meter
B – Blowout
P – Pressure Gauge
PC – Pressure
PR – Pressure Regulator
T – Temperature & Temperature Controller

Figure 6. Schematic of apparatus for SCF reaction studies.

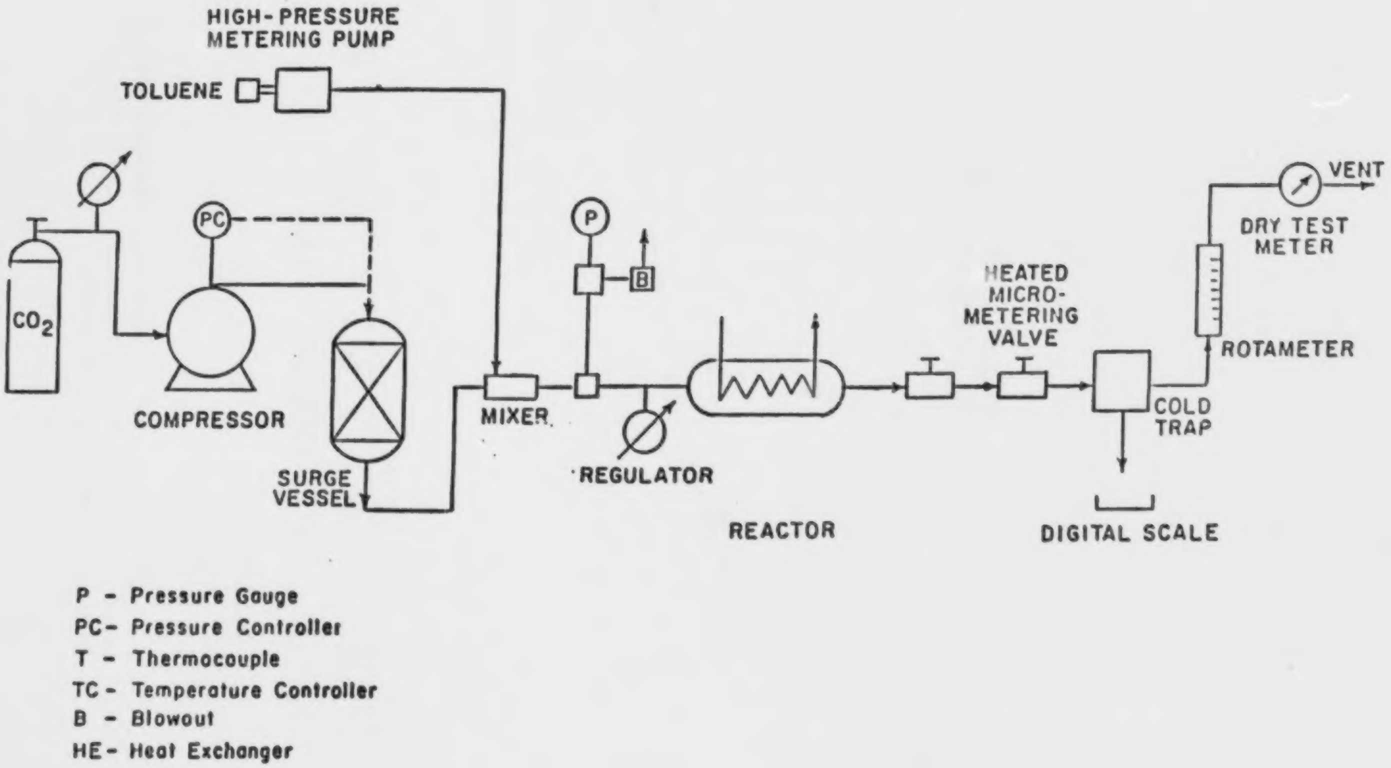

HIGH-PRESSURE METERING PUMP
TOLUENE
CO_2
PC
COMPRESSOR
SURGE VESSEL
MIXER
P
B
REGULATOR
REACTOR
HEATED MICRO-METERING VALVE
COLD TRAP
DIGITAL SCALE
ROTAMETER
DRY TEST METER
VENT
P - Pressure Gauge
PC - Pressure Controller
T - Thermocouple
TC - Temperature Controller
B - Blowout
HE - Heat Exchanger

Figure 3. Schematic of apparatus for supercritical soil extraction

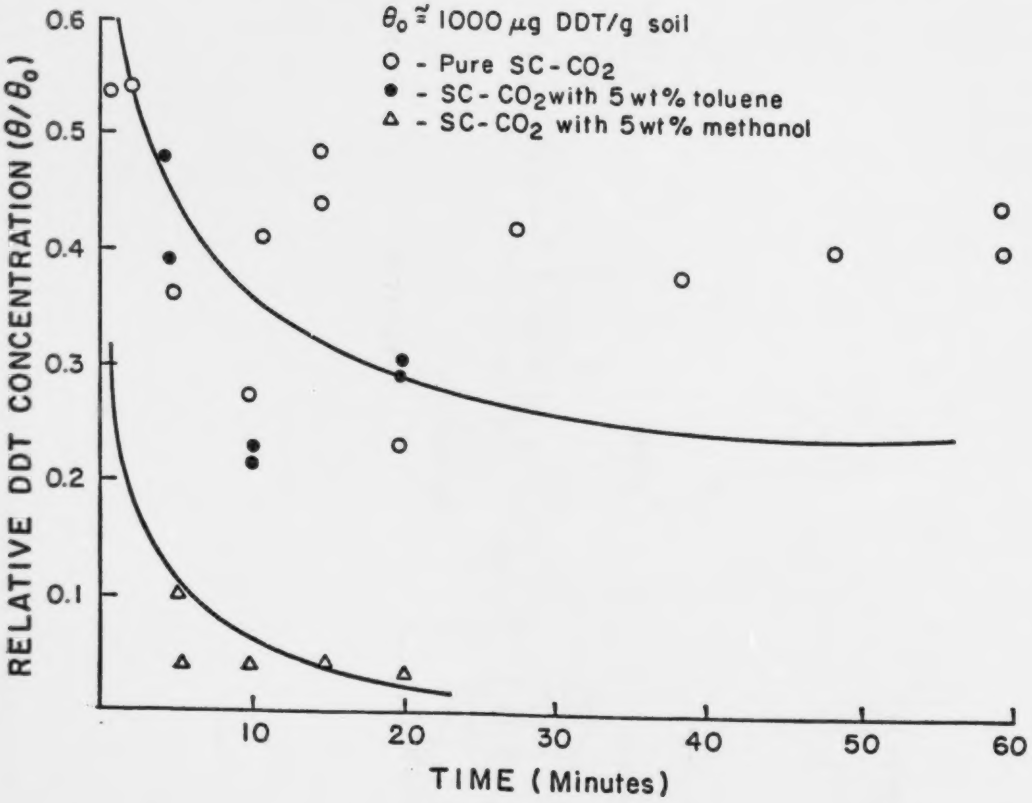


Figure 4. Temporal variation of relative soil concentration in the extraction of a DDT-contaminated, spill-site topsoil, showing the effect of entrainers.

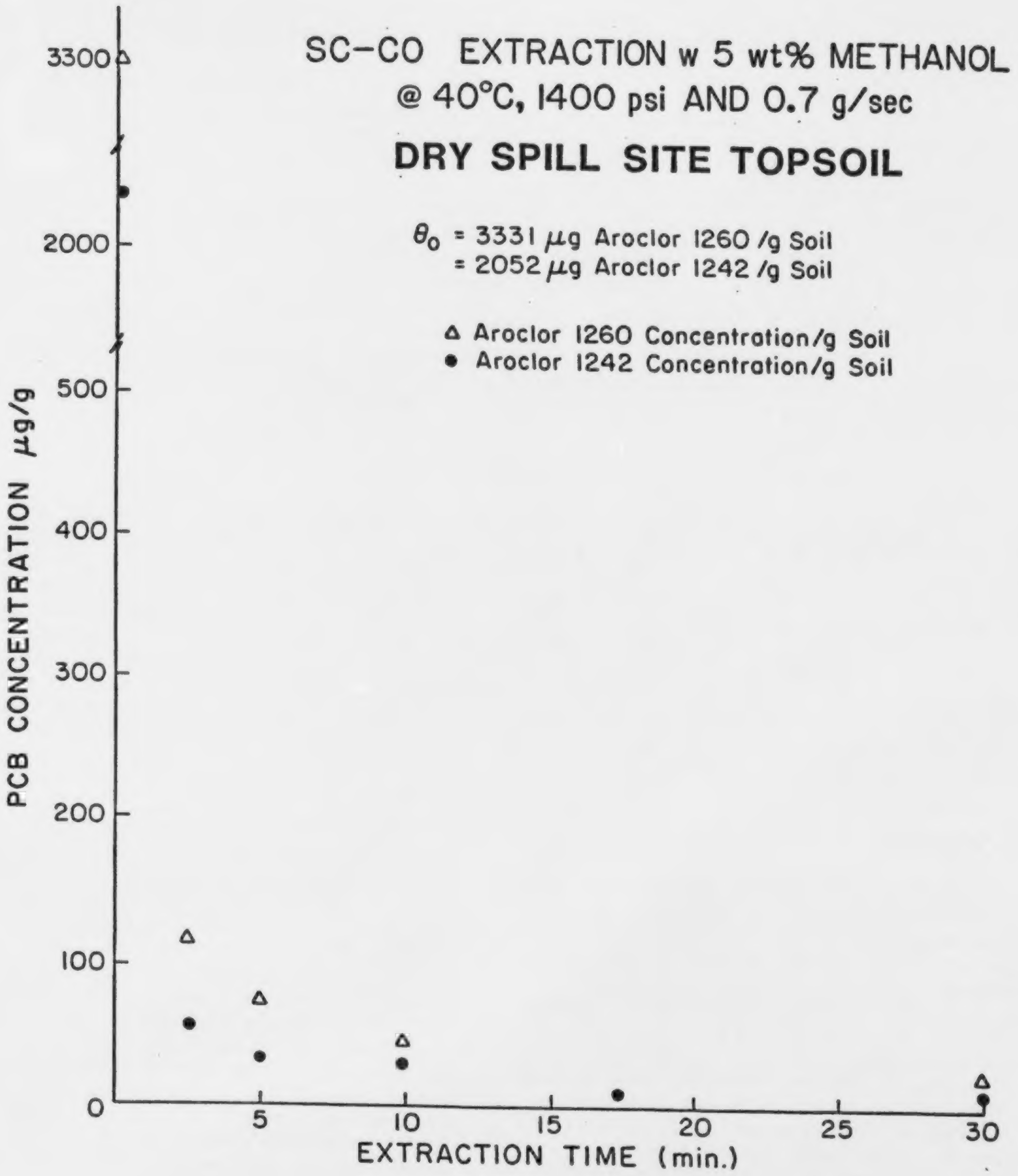


Figure 5. Temporal variation of relative soil concentration in the extraction of a PCB-contaminated, spill site topsoil.

MICROBIAL DEGRADATION OF SYNTHETIC CHLORINATED COMPOUNDS

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ABSTRACT

Pseudomonas cepacia strain AC1100 is a novel organism from the standpoint of being the product of a facilitated evolution process that has resulted in the formation of a unique metabolic pathway for the utilization of the herbicide 2,4,5-trichlorophenoxyacetic acid. A review is presented of past research pertaining to this organism as well as features it possesses that make it a highly desirable subject for further investigation. Recent results of an on-going research program designed to isolate the genetic determinants responsible for 2,4,5-T metabolism by this organism are also presented. These include the isolation of a series of spontaneous mutants affected at several different 2,4,5-T degradation-specific loci, the construction of a genomic library of AC1100 DNA sequences in *Escherichia coli* and the use of this library in the complementation of a presumed transposon *Tn5*-induced mutant.

INTRODUCTION

With growing public awareness of the health threats posed by synthetic chlorinated compounds in the environment there is an increasing demand to develop effective methods for their elimination. Microbial degradation is known to contribute to the destruction of many of these compounds in the environment. A major constraint to this process occurs, however, when appropriate dissimilatory pathways have not yet evolved in natural organisms. In this regard, it has been demonstrated that deliberate genetic selection and genetic manipulation procedures in the laboratory may lead to the construction of strains having wider biodegradative capabilities than their natural counterparts (1-5).

One of the more notable products of this form of deliberately facilitated evolution is *Pseudomonas cepacia* strain AC1100 (6). *AC1100* has acquired the ability to completely degrade the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and in the process utilize the compound as a source of carbon and energy for growth. As such, it presently provides a rather unique opportunity to study mechanisms by which genetic information may be assembled and evolve towards the formation of novel biodegradative pathways in a single organism. It has also been shown that AC1100 has the capability to degrade or dechlorinate a fairly wide variety of chlorophenol congeners although available evidence suggests that the majority of these compounds are not utilized for growth (7). Another potential use of this organism may, therefore, be as a source of genetic information in future attempts to assemble complete metabolic pathways for these compounds and other priority pollutants. Finally, treatment of contaminated soils in the laboratory with AC1100 has been found to result in significant reductions of 2,4,5-T (8,9). This organism can therefore be considered as one of the better candidates presently available for use in evaluating the effects (both in terms of treatment efficacy and environmental impact) of deliberately introducing a microorganism into the environment for the purpose of soil decontamination.

In order to fully realize both these and other potential applications of AC1100, it is clear that a good understanding of the genetics and physiology of this organism (particularly as they relate to its biodegradative capabilities) will be beneficial. The purpose of this report will be both to summarize past information that has been obtained in this regard as well as to describe ongoing studies that are being conducted in a collaborative research effort by the Gulf Breeze and Cincinnati EPA laboratories and the University of Illinois at Chicago.

PHYSIOLOGICAL STUDIES ON 2,4,5-T AND CHLOROPHENOL DEGRADATION BY AC1100

Studies have indicated that 2,4,5-trichlorophenol (2,4,5-TCP) is an early intermediate in the 2,4,5-T breakdown pathway of AC1100 and that the enzyme(s) responsible for carrying out this conversion are constitutive (10). The enzymes involved in the further breakdown of 2,4,5-TCP are as yet unknown. Proposed pathways for the degradation of 2,4-dichlorophenoxyacetic acid through a catechol intermediate (11) and pentachlorophenol through a hydroquinone (12) currently provide two alternative models for potentially describing portions of this activity (Figure 1). It also appears that one or more of the later enzymes involved in 2,4,5-T degradation by AC1100 is or are inducible (10). In this regard, the available evidence suggests that 2,4,5-TCP or a subsequent breakdown intermediate may be active as the inducer.

Considering the nature of the selective pressure employed in generating AC1000 (i.e., for growth with 2,4,5-T as a sole source of carbon and energy) it is not surprising to observe that this organism has evolved a set of enzymes that efficiently metabolize the related compound 2,4,5-TCP and are perhaps synthesized in response to this compound. The ability of AC1100 to metabolize various other chlorophenol congeners, however, may be impaired in several ways. Studies of oxygen uptake and chloride release in the presence of various chlorophenol congeners by 2,4,5-T-grown resting cells of AC1100 (Table 1) have shown that each of these compounds is dechlorinated to some degree and in many instances to an extent comparable to that of 2,4,5-TCP. In contrast, the corresponding oxygen uptake values observed for these compounds were in each case well below that observed for 2,4,5-TCP and also below the levels that might have been predicted based on their individual degrees of dechlorination. In general the more highly chlorinated congeners showed the highest ratios of dechlorination to oxygen uptake. These results suggest that to varying degrees, the dissimilation of these compounds may be blocked or impaired at steps in the process that occur after at least some dechlorination has taken place. Such a phenomenon might be expected to occur if specific intermediates formed in the initial degradation of these compounds are poorly recognized as substrates by subsequent AC1100 degradative enzymes. Particularly in the case of the more highly chlorinated phenols, it is also tempting to speculate that dechlorination may at least to some extent be mediated by hydrolytic and/or reductive mechanisms similar to those demonstrated by Steiert and Crawford (12) for pentachlorophenol (PCP) degradation by a Flavobacterium species (Figure 1).

Degradation of PCP by AC1100 has also been proposed to be constrained at the level of gene regulation. In this regard studies have revealed that, unlike 2,4,5-TCP, PCP is unable to induce its own dechlorination in resting cells of AC1100 (10). At present, the ability of other chlorophenol congeners to induce their own degradation is unknown.

Besides requiring induction, there is also some evidence to indicate that the 2,4,5-T degrading activity of AC1100 may be repressed or inhibited by a number of alternative carbon sources such as glucose, lactate and succinate (10). Under certain conditions this effect can be shown to be at least partially mediated by inhibited

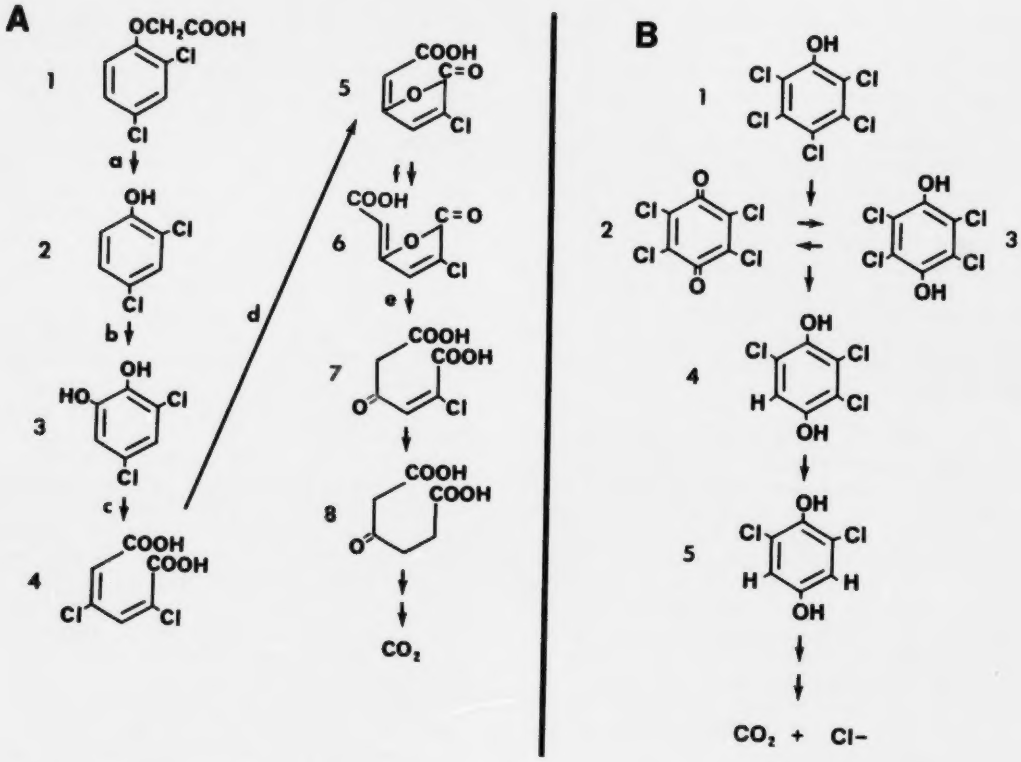

Figure 1. Pathways for 2,4-dichlorophenoxyacetic acid (2,4-D) and pentachlorophenol (PCP) biodegradation. Part A: Proposed pathway for the degradation of 2,4-D by A. eutrophus JMP134 (after Don et al., 11). The metabolites involved are: 2,4-dichlorophenoxyacetic acid, 1; 2,4-dichlorophenol, 2; 3,5-dichlorocatechol, 3; 2,4-dichloromuconic acid, 4; trans-2-chlorodiene-lactone, 5; cis-2-chlorodiene lactone, 6; 2-chloromaleylacetic acid, 7 and 3-oxoadipic acid, 8. The enzymes involved are: 2,4-D monooxygenase, a; 2,4-dichlorophenol hydroxylase, b; chlorocatechol 1,2-dioxygenase, c; chloromuconate cycloisomerase, d; 4-carboxymethylenebut-2-en-4-olide (dienelactone) hydrolase, e and trans-chlorodiene lactone isomerase, f. Part B: Proposed pathway for the degradation of PCP by a Flavobacterium sp. (after Steiert and Crawford, 12). The metabolites involved are: pentachlorophenol, 1; tetrachloro-p-benzoquinone, 2; tetrachloro-p-hydroquinone, 3; 2,3,6-trichlorohydroquinone, 4 and 2,6-dichlorohydroquinone, 5.

uptake of an inducer compound (e.g., 2,4,5-TCP). Under other conditions this effect also appears to be exerted at a step or steps in the pathway following the conversion of 2,4,5-T to 2,4,5-TCP and has been suggested to create a peculiar problem for AC1100 cells grown in the presence of 2,4,5-T and one of these alternative carbon sources. Culturing AC1100 under these conditions has been found to result in premature termination of growth, considerable loss of viability and relatively high levels of 2,4,5-TCP accumulation in the medium. The explanation proposed for these phenomena is that the inhibitory effect of the alternative substrates leads to the accumulation of 2,4,5-TCP to levels that may become toxic to the cells.

In addition to evolving the genetic information required for metabolizing 2,4,5-T, there is evidence that AC1100 has also evolved the capability to produce a 2,4,5-T emulsifying agent (13). This emulsifying agent, which the available data indicate is a high molecular weight lipid derivative, has been shown to be specific for 2,4,5-T and to some extent other

TABLE 1. CHLOROPHENOL DEGRADATION BY 2,4,5-T-GROWN AC1100 RESTING CELLS (FROM KARNS *et al*., 7)

Substrate*	Chloride Release**	Oxygen Uptake***
Dichlorophenols		
2,3-	65	16.0
2,4-	71	16.5
2,5-	84	35.9
2,6-	36	10.1
3,4-	60	27.0
3,5-	38	8.1
Trichlorophenols		
2,4,5-	90	100.0
2,3,5-	29	17.8
2,3,6-	29	2.6
2,4,6-	56	ND
2,3,4-	70	ND
3,4,5-	27	ND
Tetrachlorophenols		
2,3,4,6-	80	16.1
2,3,4,5-	60	ND
2,3,5,6-	94	ND
Pentachlorophenol	92	9.3

*Each substrate was used at a concentration of 0.1 mM. Incubation period was 3 hr.
**Percentage of the theoretical maximum.
***Expressed as a percentage of the net respiration rate observed for 2,4,5-TCP.
ND: Not determined.

related chlorophenols and is not produced by other *P. cepacia* strains. While a definite role for this compound has not as yet been established, the production of such agents is known to be important in facilitating the uptake and utilization of hydrophobic compounds by microorganisms.

MOLECULAR AND GENETIC STUDIES OF AC1100

Studies of various organisms showing the capability to degrade different synthetic compounds have revealed that the genetic information for these activities is often located on plasmids. Populations of AC1100 cells have been analyzed for plasmid content and have revealed some heterogeneity in this regard (14). It was observed that the predominant fraction of the cells (80% or more) contained a single plasmid of approximately 170 kb. A smaller fraction (about 10%) contained a plasmid of approximately 40 kb. Other plasmids ranging in size from 2 kb to 30 kb were also observed. Direct evidence for the involvement of plasmids in the 2,4,5-T degrading activity of AC1100 has not as yet been forthcoming. Efforts to cure this strain of plasmids as a means of making this determination using conventional mitomycin C treatment have not succeeded (14). The strongest indirect evidence for such involvement has resulted from the demonstration that hybridization occurs between a specific region of AC1100 plasmid DNA and a portion of the plasmid pJP4 (15). The hybridizing region of pJP4 harbors structural genes coding for both 3-chlorobenzoic acid (3CBA) and 2,4-dichlorophenoxyacetic acid (2,4-D) degradative enzymes (11). It was also reported that AC1100 plasmid DNA did not hybridize to the chlorocatechol (*clc*) gene cluster of another plasmid (pAC27) under stringent conditions (15). These *clc* genes (coding for enzymes c,d,e; Figure 1A) are both isofunctional and homologous to the corresponding genes of pJP4. This observation has lead to the conclusion that the sequence homology between AC1100 plasmid DNA and pJP4 may be limited to genes involved in the degradation of chlorophenoxy acetates (e.g., enzyme a, Figure 1A).

Further preliminary evidence concerning the location of determinants for 2,4,5-T metabolism in AC1100 has resulted from the generation of random transposon Tn5 mutants of this organism (15). Plasmid and total DNAs isolated from a number of Tn5-containing AC1100 derivatives that had also lost their 2,4,5-T degradative ability were hybridized with a labeled Tn5 DNA probe and in each case only the total DNA was found to show homology. A rigorous demonstration that the Tn5 insertions in these mutants are directly responsible for their loss of 2,4,5-T degrading activity has not yet been made. Efforts to make such a determination with one of these mutants, PT88, were pursued by the construction of a gene library of its total genomic DNA and the isolation of clones containing the kanamycin resistance determinant of Tn5 (15). Subsequent use of a flanking AC1100 DNA fragment from one side of one of these clones as a hybridization probe to filter blots of total AC1100 DNA has revealed that a sequence is present within this DNA fragment that is repeated numerous times in the AC1100 genome. These results have lead to the interesting speculation that repeated sequences may be associated with determinants for 2,4,5-T degradation in AC1100 and hence may have had a role in the evolution of this capability. In this regard, recent studies with P. cepacia strain 249 have not only identified a number of repeated insertion sequences within this organism but have also suggested a potential role for these sequences in creating genomic plasticity by processes such as insertional activation of genes as well as the recruitment of foreign plasmid-born genes by replicon fusion (16-18).

Efforts to isolate and identify the 2,4,5-T degradative genes of AC1100 are presently being continued in our laboratories. Toward this end a new genomic library of AC1100 DNA sequences has recently been constructed. To do this, total DNA from AC1100 was isolated and partially digested with restriction endonuclease Bam HI under conditions that maximized the formation of DNA fragments in the size range of 20 to 30 kb. DNA of the 23 kb broad host range cosmid vector pCP13 (19) was also digested with Bam HI (in this case to completion), dephosphorylated with calf intestine alkaline phosphatase and then ligated with the AC1100 DNA fragments. The ligation products were packaged into lambda phage heads in vitro and transfected into E. coli strain AC80. A library containing approximately 10,000 tetracycline resistant clones was generated in this manner.

The library was subsequently mobilized en masse using a modification of a previously described triparental conjugative mating system (20) into a series of 2,4,5-T defective, transposon Tn5 insertion mutants of AC1100 (15, see above). Of 12 such mutants screened in this manner, only one (PT88) was initially observed to produce tetracycline-resistant transconjugants that appeared to be phenotypically complemented based on their ability to grow on media containing 2,4,5-T as a sole carbon source. Plasmid DNA from a 2,4,5-T metabolizing transconjugant was isolated and transformed back into E. coli. This plasmid, designated pUS1, was confirmed to complement the PT88 mutation by producing nearly 100% 2,4,5-T metabolizing transconjugants when remobilized into PT88 from E. coli. The recombinant plasmid pUS1 has also subsequently been demonstrated to complement two additional mutants (PT8 and PT9) in a similar manner. Further studies are currently in progress to characterize the insert DNA of this plasmid with respect to the location, number and organization of 2,4,5-T degradative genes that it contains.

INSTABILITY OF 2,4,5-T DEGRADATIVE CAPABILITY IN AC1100

It has been documented that AC1100 cells can spontaneously lose 2,4,5-T degradative capability when grown in the absence of this compound (6). These experiments indicated that the frequency of such events may vary with culture age but could approach a rate of approximately 6×10^{-2} per cell per generation or higher. As previously mentioned, AC1100 has been shown to be effective in decontaminating 2,4,5-T treated soils in a laboratory setting. An additional observation in these studies was that cells with 2,4,5-T degradative capability rapidly disappeared from the soil samples once the 2,4,5-T levels were diminished. While not proven, it is reasonable to suggest that the instability of the 2,4,5-T degradative genes in AC1100 may have contributed significantly to this disappearance.

The underlying cause behind the instability of AC1100's 2,4,5-T degradative phenotype has not been established although several potential mechanisms can be envisaged. One obvious possibility is that 2,4,5-T determinants are located on a plasmid that is readily lost through segregation. Other possibilities include legitimate or illegitimate recombination events mediated by the presence of repeated sequences or transposable elements. As previously mentioned, numerous sequences of this type have recently been identified in P. cepacia strain 249 and it is potentially significant to note that this organism also appears to undergo spontaneous mutations at a high frequency.

The mechanism(s) underlying the spontaneous loss of 2,4,5-T degradative ability by AC1100 are currently under further investigation in our laboratories. A number of spontaneous mutants have been identified by replica plating AC1100 colonies grown on a nonselective medium (containing basal salts and 0.1% yeast extract, 6) onto medium containing 2,4,5-T as sole carbon source. It has been observed that these mutants can be phenotypically differentiated on the basis of their growth charac-

TABLE 2. GROWTH CHARACTERISTICS OF SPONTANEOUS AC1100 MUTANTS

	Growth Substrate		
Mutant Class	2,4,5-T	Glucose	2,4,5-T + Glucose
A	no growth	comparable to wild-type	comparable to wild-type but produces a dark red pigment
B	no growth	comparable to wild-type	very little or no growth
C	no growth	comparable to wild-type	comparable to wild-type
D	no growth	comparable to wild-type but colonies are more mucoid	comparable to wild-type but colonies are more mucoid

teristics in basal salts medium containing 2,4,5-T plus glucose. These differences which are summarized in Table 2 suggest that multiple genetic loci may be independently susceptible to spontaneous mutational events in AC1100. In view of this observation it appears unlikely that the loss of a plasmid can be the sole explanation for loss of 2,4,5-T degrative capability in this organism.

Studies are currently in progress to both identify the steps in the 2,4,5-T degradative pathway at which these mutants are blocked and to isolate the affected genes by means of complementation with our AC1100 genomic library. As the cloned DNA sequences corresponding to these mutated regions are isolated, it should be possible to use them as hybridization probes in determining the physical basis for the mutational events.

ACKNOWEDGEMENTS

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BACTERIAL OXIDATION OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

The present studies represent a summary of the results obtained on the degradation of polychlorinated biphenyls by two strains of bacteria. The organisms, Alcaligenes eutrophus H850 and Pseudomonas putida LB400, are capable of metabolizing a wide range of PCB congeners. The initial reactions involved in the oxidation of 2,5,2',5'-tetrachlorobiphenyl by both organisms appears to involve oxidation at the unsubstituted 3,4-positions. The properties of the enzymes involved in these reactions and the regulation of their activities are being studied by modern molecular biological techniques. It is anticipated that the results obtained will lead to the construction of improved strains of bacteria that can efficiently degrade a wide range of PCB congeners.

INTRODUCTION

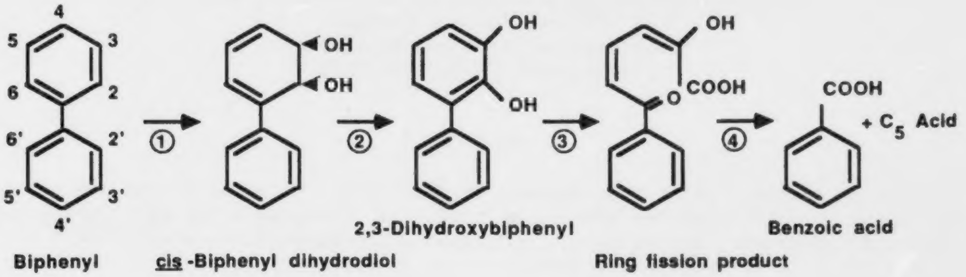
Polychlorinated biphenyls (PCBs) are manufactured by the controlled chlorine substitution of the biphenyl molecule. Mixtures of PCB isomers and congeners of a differing degree of chlorine substitution were first marketed in the USA under the name "Aroclor" by the Monsanto Corporation almost 50 years ago.

PCBs are extremely stable compounds, their excellent heat resistance and dielectric properties have led to wide industrial use in capacitors, transformers, dielectric fluids, fire retardants and plasticizers (10,12).

The stability of PCBs also makes them quite resistant to biodegradation. This is particularly true for congeners containing 5 or more chlorine substituents (7,12) which tend to accumulate in the environment. The lipophilic nature of PCBs causes them to partition into the fatty tissue of higher organisms, thus concentrating them in the food chain by several orders of magnitude at each succeeding trophic level. This is of concern to human health since the long term effects of PCBs are not fully understood.

Two microorganisms, Alcaligenes eutrophus strain H850 and Pseudomonas putida strain LB400 were used in this study. Both organisms were isolated from PCB contaminated soil and tested for their ability to degrade a wide range of PCBs (1,2,4) including congeners that have no unsubstituted 2,3-positions (the favored sites of initial oxidative attack), such as 2,5,2',5'-tetrachlorobiphenyl (2,5,2',5'-CB). Congener depletion assays indicate that chlorine substitution at the 2,5-positions may facilitate degradation of certain PCBs (2,3). The pathway used for the degradation of a 2,5-dichlorinated aromatic ring has not been established.

However, it seems possible that alternative pathways to that shown in Figure 1 for biphenyl may exist. The general features of the pathway have often been extrapolated to account for the biodegradation of certain PCB congeners (7,12). For example, it is generally assumed that the initial oxidative reaction occurs by the incorporation of both atoms of molecular oxygen into the aromatic nucleus that contains the least number of chlorine substituents. The resulting dihydrodiol is then oxidized by a pyridine nucleotide-dependent dehydrogenase to form the appropriate ring-fission substrate. Subsequent steps involving hydrolysis, hydration and aldol cleavage are thought to account for the formation of small molecules that can enter the tricarboxylic acid cycle. It is difficult to see how 2,5,2',5'-CB and similar PCBs can be degraded by this pathway. The results presented, show for the first time that bacteria can initiate oxidation of the biphenyl molecule at the 3,4-positions.



① Biphenyl dioxygenase
② cis-Biphenyl dihydrodiol dehydrogenase
③ 2,3-Dihydroxybiphenyl dioxygenase
④ Hydrolyase

Figure 1. Initial reactions in the oxidation of biphenyl by *A. eutrophus* H850 and *P. putida* LB400

MATERIALS AND METHODS

Microorganisms and growth conditions

Alcaligenes eutrophus strain H850 and *Pseudomonas putida* strain LB400 were isolated as described previously (1,4). Transformation studies were usually conducted with biphenyl-induced cells. Metabolites were isolated by high pressure liquid chromatography (HPLC) and identified from the information provided by conventional chemical techniques. These included proton magnetic resonance spectrometry (PMR), mass spectrometry (MS) and gas chromatography (GC). In certain instances crude mixtures of metabolites were separated and identified by GC/MS.

Mutant Isolation

Mutagenesis with N-methyl-N'-nitro-N-nitrosoguanidine was carried out as described previously (5). Transposon mutagenesis was carried out using either *E. coli* NEC0100 (pRKTV14) as described by Finette (6) or *E. coli* C600 (pBEE-132) as described by Kuner et al (11). Presumptive biphenyl^{-} strains were selected on the basis of their failure to produce large colonies when grown on mineral salts agar containing 0.2% succinate and 40 microgram (μ g/ml) of triphenyltetrazolium chloride. Biphenyl crystals were placed in the lid of each petri dish.

Rapid screening techniques were utilized to identify mutants defective in structural genes of the biphenyl catabolic pathway. Biphenyl dioxygenase activity was detected by the ability of strains to clear zones of biphenyl from the surface of agar plates that had been sprayed with an ether solution of biphenyl.

Mutants defective in cis-2,3-dihydroxy-2,3-dihydrobiphenyl dehydrogenase and 2,3-dihydroxybiphenyl dioxygenase were detected by their ability to clear zones of biphenyl from the surface of agar plates as described above. Dehydrogenase mutants were distinguished from dioxygenase mutants by their ability to form a yellow ring fission product when colonies on agar plates were sprayed with an ether solution of 2,3-dihydroxybiphenyl. No color change was observed when 2,3-dihydroxybiphenyl dioxygenase mutants were exposed to 2,3-dihyroxybiphenyl. Mutants defective in the ring fission enzyme, 2-hydroxy-6-oxo-phenylhexa-2,4-dienoic acid hydrolase, were detected by the accumulation of the yellow ring fission product when colonies were exposed to biphenyl, *cis*-2,3-dihydroxy-2,3-dihydrobiphenyl and 2,3-dihydroxybiphenyl.

RESULTS

Whole cell studies

Both *Alcaligenes eutrophus* H850 and *P. putida* LB400 were able to utilize biphenyl as the sole source of carbon and energy for growth. In order to establish the initial reactions involved in biphenyl degradation mutant strains were isolated that contained defects in the structural genes for the first four enzymes of the pathway shown in Figure 1. The properties of these mutant strains are shown in Table 1. Strains FM200 and FM202 do not produce clear zones on agar plates that have been sprayed with an ether solution of biphenyl. However, crossfeeding experiments with *Beijerinckia* B8/36, a mutant that accumulates *cis*-biphenyl dihydrodiol (8), results in growth of both FM200 and FM202. These strains may have defects in the structural gene(s) for biphenyl dioxygenase or they may be unable to transport biphenyl. Strains FM203, 204, and 408 each oxidize biphenyl to *cis*-biphenyl

TABLE 1. PRODUCTS FORMED FROM BIPHENYL BY MUTANT STRAINS

OF *P. PUTIDA* LB400[1]

Strain Designation	Source	Products formed from Biphenyl
FM200	*Tn5* Km^{r}[2]	None
FM202	*Tn5* Km^{r}	None
FM203	*Tn5* Km^{r}	*cis*-Biphenyl dihydrodiol
FM204	*Tn5* Km^{r}	*cis*-Biphenyl dihydrodiol
FM408	NTG[3]	*cis*-Biphenyl dihydrodiol
FM903	*Tn5*-132 tet^{r}[4]	2,3-Dihydroxybiphenyl (2,3-DB)
FM905	*Tn5*-132 tet^{r}	2,3-Dihydroxybiphenyl (2,3-DB)
FM205	*Tn5* Km^{r}	2,3-DB Ring fission product
FM206	*Tn5* Km^{r}	2,3-DB Ring fission product

[1] Strains were isolated as described in Materials and Methods.

[2] Kanamycin resistant.

[3] N-methyl-N'-nitro-N-nitrosoguanidine.

[4] Tetracycline resistant.

dihydrodiol which has an absorbtion maximum at 303 nm (8). Biphenyl and cis-biphenyl dihydrodiol are both oxidized by strains FM903 and 905 to a compound that shows an absorption maximum at 247 nm. In addition, cell free supernatant solutions containing this metabolite are rapidly oxidized to a yellow ring fission product by biphenyl-induced cells of the parent strain of P. putida LB400. These observations strongly indicate that strains FM903 and 905 contain a defective gene for 2,3-dihydroxybiphenyl dioxygenase and that the product formed from biphenyl and cis-biphenyl dihydrodiol is 2,3-dihydroxybiphenyl. When biphenyl, cis-biphenyl dihydrodiol and 2,3-dihydroxybiphenyl are incubated with strains FM205 and 206 a bright yellow ring fission product which has an absorbance maximum at 434 nm accumulates from each substrate. These results show that neither strain contains an active enzyme for the metabolism of the ring-fission product formed from 2,3-dihydroxybiphenyl. The results are consistent with the pathway shown in Figure 1. Polarographic studies indicate that A. eutrophus H850 also utilizes this pathway (data not shown).

Oxidation of PCB congeners by biphenyl-induced cells of A. eutrophus H850 and P. putida LB400

Previous studies have shown that congener depletion assays can provide valuable information on the ability of different bacterial strains to oxidize individual PCBs (1,2,3,4). The results of these investigations are summarized in Table 2. Quantitative analysis of the data is difficult due to the fact that percentage depletion was only measured at one time point (24h) and that the data represents a summation of several different experiments. Nevertheless, the results clearly indicate that chlorine substitution at the 4,4'-positions renders a molecule less susceptible to degradation by these strains and that P. putida LB400 is more effective than A. eutrophus H850 in oxidizing congeners with this substitution pattern (Table 2B). The effect of chlorine substitution at the 2,6-positions is shown in Table 2C. This substitution pattern seems particularly effective in preventing significant PCB degradation by both organisms. In contrast, a 2,5-dichlorophenyl ring improves degradability, even for congeners that contain 1-3 chlorine substituents on the other ring (Table 2D).

Oxidation of 2,5,2',5'-tetrachlorobiphenyl (2,5,2',5'-CB)

Alcaligenes eutrophus H850 and Pseudomonas putida LB400 were unable to utilize 2,5,2',5'-tetrachlorobiphenyl as a source of carbon and energy for growth. However, biphenyl-grown cells of both organisms rapidly transformed this tetrachlorobiphenyl to polar products.

The first product formed from 2,5,2',5'-CB was isolated and identified by conventional chemical techniques as 3,4-dihydroxy-3,4-dihydro-2,5,2',5'-tetrachlorobiphenyl (3,4-dihydrodiol). Subsequent metabolism of this dihydrodiol led to the accumulation of a more polar product which appeared to be resistant to further degradation. This metabolite was isolated and identified as 3,4,3',4'-tetrahydroxy-3,4,3',4'-tetrahydro-2,5,2',5'-tetrachlorobiphenyl (bis-3,4-dihydrodiol). There were no indications of prior dechlorination reactions which would leave 2,3-positions available for oxidation. However, the identification by GC/MS of 2,5-dichloroacetophenone as a minor metabolite confirms the studies of Bedard et al (3), and may indicate the presence of a novel pathway for the degradation of biphenyls that contain certain chlorine substitution patterns.

The second reaction in the bacterial degradation of biphenyl is catalyzed by a pyridine nucleotide-dependent dehydrogenase which oxidizes cis-2,3-dihydroxy-2,3-dihydrobiphenyl to 2,3-dihydroxybiphenyl. This enzyme was very active in cell extracts prepared from biphenyl-grown cells of A. eutrophus H850 and P. putida LB400 (data not shown). The same cell extracts were not active against the 3,4-dihydrodiol or the bis-3,4-dihydrodiol.

DISCUSSION

A. eutrophus H850 and P. putida LB400 can use biphenyl as a sole source of carbon and energy for growth. Preliminary studies with the mutants listed in Table 1 indicate that P. putida LB400 oxidizes

TABLE 2. DEGRADATION OF PCB CONGENERS BY *A. EUTROPHUS* H850 AND *P. PUTIDA* LB400[1]

A

PCB Congener	Percent degraded	
	H850	LB400
2,3-	100	100
2,5-	100	100
2,6-	30	40
2,2'-	100	100
2,4'-	100	100
4,4'-	40	50
2,4,4'-	75	100
2,5,2'-	100	100
2,5,4'-	100	100
2,4,2',4'-	55	100
2,4,3',4'-	20	65
2,4,6,4'-	0	0
2,5,2',3'-	100	100
2,5,3',4'-	90	100
2,4,6,2',4'-	0	0
2,3,4,2',5'-	60	100

B

PCB Congener	Percent degraded	
	H850	LB400
4,4'-	40	50
2,4,4'-	75	100
2,4,2',4'-	55	100
2,4,3',4'-	20	65
2,4,6,4'-	0	0
3,4,3',4'-	0	0
2,4,6,2',4'-	0	0
2,4,5,2',4',5'-	15	70

C

PCB Congener	Percent degraded	
	H850	LB400
2,6-	30	40
2,4,6-	20	25
2,4,6,4'-	0	0
2,6,2',6'-	0	0
2,4,6,2',4'-	0	0
2,4,6,3',4'-	0	0
2,4,6,3',5'-	0	0
2,3,6,2',3',6'-	20	35
2,4,6,2',4',6'-	0	0

D

PCB Congener	Percent degraded	
	H850	LB400
2,5-	95	100
2,5,2'-	100	100
2,5,4'-	100	100
2,5,2',3'-	100	100
2,5,3',4'-	90	100
2,5,2',6'-	90	100
2,5,2',5'-	100	100
2,5,2',4',6'-	40	75
2,5,2',4',5'-	70	100
2,5,2',3',4'-	60	100

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[1] Data obtained from defined congener assays as described in (2) and reported in part in references 3 and 4. Each mixture contained 10-11 chlorinated biphenyls in which each congener was present at a concentration of 5.0 µM.

biphenyl at the 2,3-position to form cis-2,3-dihydroxy-2,3-dihydrobiphenyl. Subsequent oxidation of this metabolite follows the reaction sequence shown in Figure 1. A mutant strain of A. eutrophus H850 (Strain FM803) also oxidizes biphenyl to cis-2,3-dihydroxy-2,3-dihydrobiphenyl and polarographic studies with biphenyl-grown cells of the parent organism (data not shown) indicates that the pathway shown in Figure 1 also represents the major reaction sequence for the oxidation of biphenyl by A. eutrophus H850.

The results in Table 2 show that both A. eutrophus H850 and P. putida LB400 have the ability to oxidize a wide range of PCB congeners. Strain LB400 appears to be more effective than strain H850 in terms of the extent of oxidation of individual PCBs. However, this aspect has not been investigated in detail. In general terms, the results shown in Table 2 indicate that a 2,5-chlorine substitution pattern enhances degradation and this feature has been reported in some detail by Bedard et al (3). In contrast a 4,4'- or 2,6-chlorine substitution pattern inhibits oxidation even if the molecule has free 2,3-positions available for oxygenation.

Since both organisms oxidized 2,5,2',5'-tetrachlorobiphenyl (2,5,2',5'-CB) this substrate was chosen for further study. The results obtained are shown in Figure 2. The major reactions involve sequential dihydroxylation at both of the open 3,4-positions in 2,5,2',5'-CB.

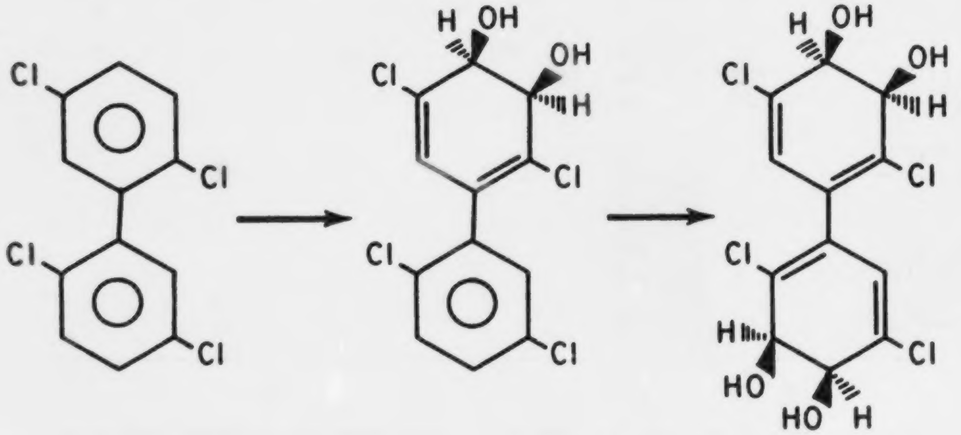

Figure 2. Major reactions involved in the transformation of 2,5,2',5'-CB by biphenyl-grown cells of A. eutrophus H850 and P. putida LB400. The formation of the minor metabolite, 2,5-dichloroacetophenone is not shown.

The relative stereochemistry of the hydroxyl groups in both products has not been firmly established. The cis orientation(s) shown in Figure 2 is based on the results of previous studies which have shown that bacteria initiate the oxidation of biphenyl and several other aromatic hydrocarbons by enzymatically incorporating both atoms of oxygen into the aromatic nucleus to form dihydrodiols in which the hydroxyl groups have a cis-relative stereochemistry (9).

There are several possible explanations for the results obtained in this study. At the enzyme level, different chlorine substitution patterns cause steric effects and these could permit or retard access of different PCBs to the active site of the dioxygenase induced by biphenyl. Thus the oxidation of 2,5,2',5'-CB at the 3,4-positions may be catalyzed by the 2,3-dihydroxybiphenyl dioxygenase that is induced by growth in the presence of biphenyl. Alternatively, a different biphenyl oxygenase may be responsible for the observed results. Different chlorine substitution patterns may be responsible for effects at the transcriptional level. For example, a 2,5-substitution pattern could induce an enzyme with different properties and substrate specificity to the enzyme induced by biphenyl. The difficulties associated with the interpretation of the results are due to the low levels of substrates used and the length of time required to demonstrate significant degradation of individual PCB congeners. Studies currently being conducted are directed towards the elucidation of these problems. As described in the present study mutants have been isolated that are defective in the structural genes for the first four enzymes of the biphenyl degradative pathway. The use of these organisms in biotransformation experiments should provide valuable information on the pathways utilized for the oxidation of different PCB congeners.

Our future studies will be directed towards cloning the genes for biphenyl dioxygenase into high expression vectors. The availability of such strains will facilitate the isolation and characterization of the initial dioxygenase and permit unambiguous determination of the substrate specificity of the enzyme for individual PCB isomers and homologs. In addition, such studies will provide valuable information on the regulation of the enzyme(s) involved in PCB metabolism. We anticipate that this approach will lead to the construction of bacterial strains that can efficiently biodegrade complex mixtures of PCBs.

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ENGINEERING P450 GENES IN YEAST

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ABSTRACT

Cytochrome P450 systems catalyze the monooxygenation of a broad range of xenobiotic compounds. These systems are most extensively characterized in mammals, where for a given species a single form of NADPH-cytochrome P450 oxidoreductase (P450R) donates reducing power to any of 30-to-100 unique members of a P450 protein superfamily. We are interested in gene engineering P450 systems in yeast for the oxidative detoxication and biodegradation of environmentally stable organic pollutants. Two organisms, *Saccharomyces cerevisiae* (baker's yeast) and *Candida tropicalis* ATCC750, a yeast capable of *n*-alkane assimilation, have been used as models. *S. cerevisiae* is particularly useful for gene manipulation; *C. tropicalis* is of interest for its possible advantages for genetically engineering the uptake and catabolism of hydrophobic toxicants. The major proteins of interest in these model yeasts are: P450R; the P450 lanosterol 14α-demethylase, involved in sterol biosynthesis; and P450 *n*-alkane ω-hydroxylase.

Genes for these proteins have been isolated and determination of their DNA sequence has been completed or is in progress. Amino acid sequences deduced from these DNAs were compared to sequences reported for mammalian P450 system proteins. Our results indicate that the P450R protein is highly conserved among yeast and mammals. The yeast P450 proteins share patterns observed for mammalian P450s, with sequence similarity among enzymes of similar function and with wide sequence diversity between P450s of different substrate specificity. The yeast P450s for lanosterol demethylation and alkane *n*-hydroxylation belong to two new families in the P450 superfamily. Characterization of these genes forms a basis for the gene engineering of P450 expression in yeasts.

INTRODUCTION

Viewed broadly in terms of the natural cycles in the biosphere it is clear that nearly all compounds are degraded. These biological degradations are primarily effected by bacteria, yeasts, molds and other microorganisms. Included in the biodegradable category are a variety of halogenated aromatic compounds. Thus when environmental persistence of various polychlorinated aromatic hydrocarbons is encountered, it is reasonable to consider the isolation or modification of such organisms in order to catalyze the entry of these persistent compounds into the pre-existing degradative pathways. Numerous national workshops and symposia have proposed the development of microbial biodegradation technologies for their potential as low cost, environmentally sound tools in the treatment of high priority pollutant targets in land fills, waste sites, and industrial effluents. (13,9).

Because of the highly substituted structure of the persistent polychlorinated aromatics, the P450 monooxygenases are likely candidates as catalysts for their specific oxidation or reductive dechlorination. Fungi and yeasts are eukaryotic microorganisms which are known to catalyze a broad range of these reactions using

P450 enzymes (10) and mammalian P450s have been implicated in the degradation of such compounds as 2,3,7,8-tetrachlorodibenzo-p-dioxin (8,4), 2,3,7,8-tetrachlorodibenzofuran (7), and hexachlorobenzene (12). We are interested in gene engineering yeasts to provide organisms combining both the P450-catalyzed degradation of persistent toxic compounds and the capacity to survive or to survive and grow in contaminated environments.

PURPOSE AND APPROACH

Fig. 1 shows a diagram of a cytoplasmic membrane-bound P450 monooxygenase system. In mammals as many as 30-to-100 different P450s make up the P450 protein superfamily (5). Each P450 receives electrons for its reaction from a single NADPH-P450 oxidoreductase (P450R), or in some cases from P450R plus a second donor, cytochrome b5. The individual P450 enzymes provide the specificity for a broad range of oxidative reactions, shown here as the hydroxylation of the substrate with the concomitant formation of a water molecule.

Until recently the molecular genetics of eukaryotic P450s was based entirely upon studies of mammalian systems. Although major P450 enzymes had been described for yeasts (2), none of the relevant genes or the signals controlling expression of those genes were characterized. Since an understanding of these genetic elements would provide a basis for engineering P450s in yeasts, the goal of this phase of our work has been the isolation and molecular characterization of genes coding for yeast P450 systems. Two organisms were used: baker's yeast, *Saccharomyces cerevisiae*; and *Candida tropicalis* ATCC750. *S. cerevisiae* is highly characterized genetically and has become the eukaryotic microorganism of choice for the application of molecular genetic techniques. *C. tropicalis* ATCC750 is representative of a group of yeasts capable of growth upon *n*-alkanes in petroleum as a carbon and energy source; such yeasts already express lipophilic properties which may be useful in gene engineering cells for the uptake and metabolism of hydrophobic hazardous compounds.

The major proteins of interest in both of these yeasts are P450R and the P450 enzyme lanosterol 14α-demethylase (14DM), an enzyme well studied for its role in the biosynthesis of ergosterol. Additionally *C. tropicalis* employs the P450 enzyme ω-hydroxylase (P450alk) as catalyst of the initial step in *n*-alkane catabolism. In the recently recommended nomenclature for the P450 gene superfamily, 14DM and P450alk are designated as LIA1 and LIB1 respectively (6).

RESULTS

Progress in our isolation and DNA sequence characterization of these genes has been described (3,1,11, and manuscripts submitted for publication) and is summarized in Table I. Access to the DNA sequence of a gene makes possible the description of the deduced amino acid sequence of the encoded protein. Thus this summary Table I also indicates that we have full or partial data for the deduced amino

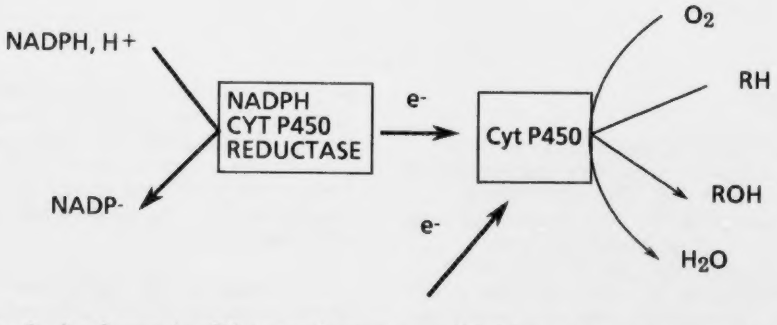

Fig. 1. A schematic of the membrane bound P450 monooxygenase system.

Table 1. PROGRESS IN THE CHARACTERIZATION OF YEAST P450 GENES

Organism	Genes Isolated	Genes Sequenced	References
S. cerevisiae			
P45014DM LIA1*	X	X	Kalb *et al.*, 1986 Kalb *et al.*, manuscript submitted Kalb and Loper, manuscript submitted
P450R	X	in progress	Sutter *et al.*, unpublished
C. tropicalis			
P450alk LIB1*	X	X	Sanglard *et al.* 1987 Sanglard *et al.*, manuscript in preparation
P45014DM	X	in progress	Chen *et al.*, unpublished
P450R	X	in progress	Sutter *et al.*, unpublished

*Nomenclature of Nebert *et al.*, see ref. 6.

acid sequence of each of these proteins. We have now begun to ask how these lower eukaryotic P450R and P450 proteins compare to the P450 system proteins in the P450 superfamily. Results of such comparisons are presented here.

Our first test was to compare the deduced amino acid sequence of one mammalian P450 with all available protein sequences. Bovine adrenal cortex P450C21 was arbitrarily chosen for the mammalian P450 sequence. The pool of protein sequences contained all of the several thousand sequences in the National Biomedical Research Foundation (NBRF) Protein Sequence Data Bank Release 10.0, our data for two yeast P450 proteins, and sequence data for three mammalian P450s not yet included in the NBRF compilation. The yeast P450 sequences were for *S. cerevisiae* 14DM and *C. tropicalis* P450alk. The algorithm used was that of Wilbur and Lipman (14) implemented at Bionet (The parameters used were: WORD-LENGTH, 1; GAP-PENALTY, 2; WINDOW, 30; DENSITY, Less; and FAST, No).

These comparisons appear as relatedness scores in Fig. 2. The majority of proteins of course show only random sequence relatedness; for the total population the mean score was 4.6 +/- 0.9 s.d. The horizontal bar covers the location of all 22 of the eukaryotic P450s in this distribution and illustrates the wide diversity of protein sequence structure among the P450 superfamily. Five entries are plotted with values of >60; one of these is for the P450C21 protein itself. The relatedness scores for the remaining 17 P450s in this population range from 60 down to 19, a score four times that of random relatedness. The relatedness scores of *S. cerevisiae* 14DM and *C. tropicalis* P450alk, indicated as *S. c.* and *C. t.* in Fig. 2, are 20 and 29 respectively. Although relatively low, these scores are similar to the score seen with bovine P450scc (score = 19). Thus these two P450s from the lower eukaryotes lie within the diversity range of the mammalian P450s.

Homology and diversity among yeast P450s. A relatedness score as discussed above gives an overall average for two protein sequences. Homology matrix comparisons between pairs of

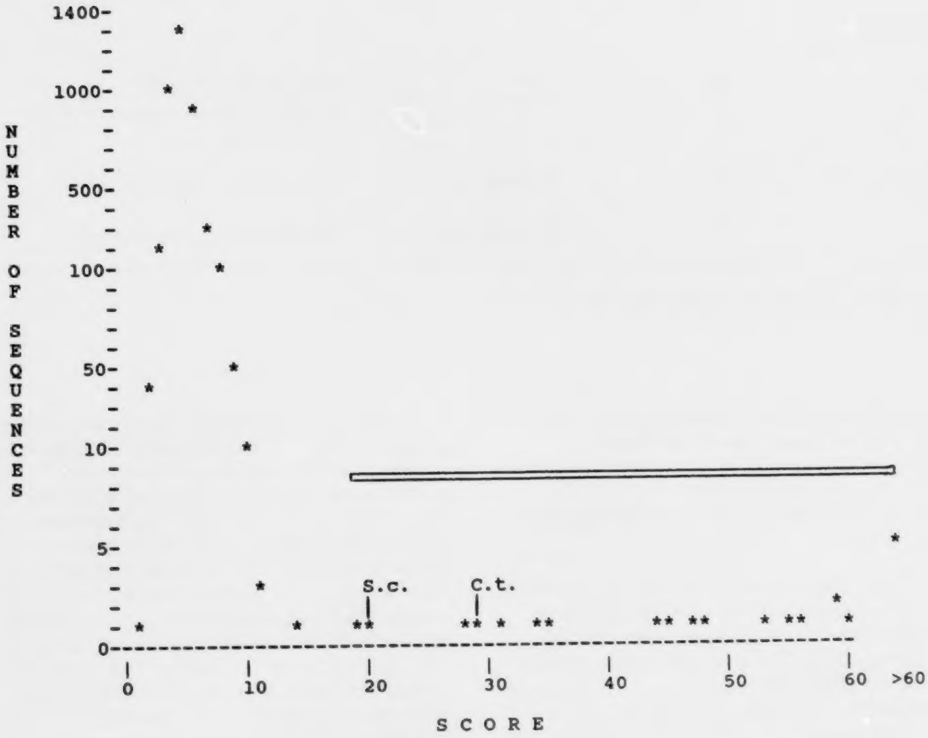

Fig. 2. Relatedness scores of P450C21 with the sequences in the National Biomedical Research Foundation protein database.

P450s allow the examination of the localization of similarities and differences across the length of the amino acid sequences. Such comparisons were obtained using the Pustell dot matrix program (International Biotechnologies, Inc.; the parameters used were: RANGE, 6; SCALE, 0.9; HASH LEVEL, 1; JUMP LEVEL, 1; STEP, 1; MINIMUM VALUE, 40; COMPRESSION, 5.) Regions of homology between paired sequences are indicated by the presence of a letter which encodes a score proportional to the degree of homology: A = 100%, B = 98-99%, Z = 50-51%, a = 48-49%, b = 46-47% etc. Thus in this program a self-comparison for any amino acid sequence would generate a diagonal plot consisting of a continuous string of A's.

Our data of deduced amino acid sequence for the 14DM genes from both *S. cerevisiae* and *C. tropicalis* were used to examine the relatedness of this P450 in the two yeast genera. Since the present DNA sequence characterization of the *C. tropicalis* 14DM gene contains a few ambiguous bases, the homology matrix comparison which resulted is only a close approximation. However it is clear from the pattern obtained that these two proteins have extensive homology throughout their deduced amino acid sequences, see Fig. 3A.

This homology for the 14DM proteins is in marked contrast to the minimal relatedness seen between the two *C. tropicalis* P450s, 14DM and P450alk, see Fig. 3B. Again the homology matrix comparison of these two proteins is only a close approximation, pending resolution of a few ambiguous nucleotide residues in our present DNA sequence for the *C. tropicalis* 14DM gene. This lack of pattern structure reveals a remarkable sequence diversity for these two P450s from the same yeast.

2. P450R proteins

Determination of the DNA sequence for the P450R gene from *C. tropicalis* is nearly complete and sequencing of the *S. cerevisiae* P450R gene is in progress. Preliminary data indicate that these P450R proteins are quite similar in protein sequence and also show high homology to mammalian P450R proteins.

DISCUSSION

Isolation and DNA sequence determination of the P450 genes for 14DM of *S. cerevisiae* and for P450alk of *C. tropicalis* has allowed the first comparisons of deduced protein sequences for P450s of lower and higher eukaryotes. We have shown that each of these P450s is a member of a distinct P450 family (Kalb *et al.* manuscript submitted for publication 1987, Sanglard *et al.*, unpublished). Together with the preliminary homology comparisons presented here involving the *C. tropicalis* 14DM sequence, the data strongly support the conclusion that P450 structure in yeasts resembles mammalian P450 structure. The two yeast 14DM P450s show extensive homology, and in results not presented here we have demonstrated that the 14DM gene of *C. tropicalis* is functionally expressed in *S. cerevisiae* and can compensate for 14DM-deficient mutants in that yeast (C. Chen *et al.*, unpublished). On the other hand, comparisons of P450alk with deduced sequences of 14DM of either yeast show great diversity, an observation which is consistent with the diversity between these P450s regarding substrate and reaction specificity. That the structure for P450R protein is highly conserved across yeasts and mammals is of particular interest, since molecular genetic tools for a detailed structure function analysis can be applied to the yeast enzyme as a model of all eukaryotic P450R, including human.

Access to this DNA sequence data makes possible the molecular genetic manipulation of these genes. For example, based upon DNA sequence information T. Turi has inactivated the 14DM gene in *S. cerevisiae* by gene disruption, an experiment which showed that this gene is essential for normal growth (Kalb *et al.*, manuscript submitted for publication, 1987). The availability of such genetically inactivated strains provides an ideal background for tests in which restoration of activity can be examined under genetically altered levels of expression. Also, the normal P450 gene can be mutated *in vitro* and the altered construct put into the tester strain and its level of function determined. Access to the DNA sequence of the *C. tropicalis* gene for P450alk will facilitate our testing of its expression as a foreign gene in *S. cerevisiae*. Experiments using these methods form important steps toward gene engineering other specific P450s in yeasts for the degradation of hazardous wastes.

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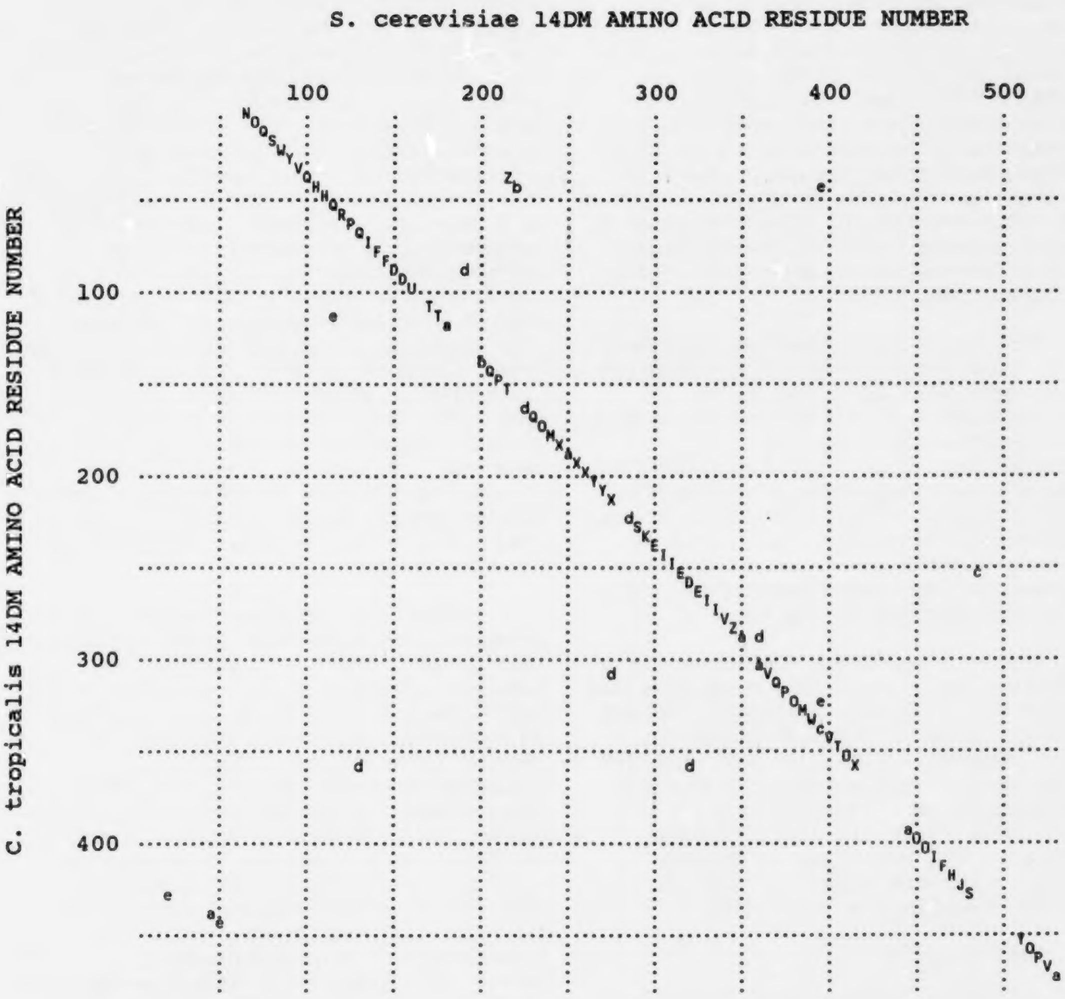

Fig. 3A. Homology matrix comparisons of P45014DM from two yeasts.

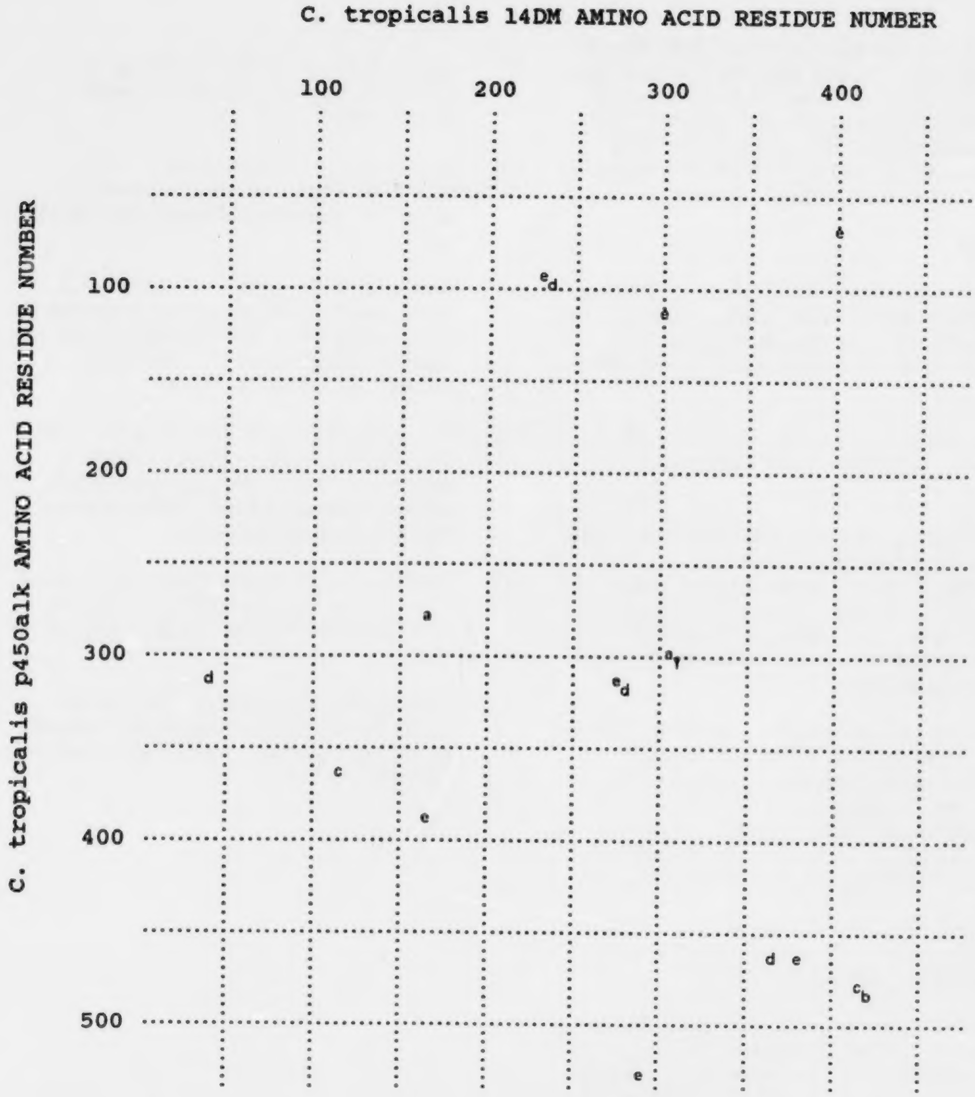

Fig. 3B. Homology matrix comparisons of two P450s from *C. tropicalis* ATCC750.

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BIODEGRADATION OF ORGANOPOLLUTANTS BY PHANEROCHAETE CHRYSOSPORIUM: PRACTICAL CONSIDERATIONS

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ABSTRACT

We previously reported that a wide variety of structurally diverse organopollutants are mineralized by the lignin degrading system of the white rot fungus Phanerochaete chrysosporium (Science 228, 1434, 1985). Current research is directed towards application of this technology for the biodegradation of environmental pollutants and hazardous wastes. The system is effective in both liquid and solid matrices. Bulking agents such as wood chips or corn cobs can also serve as a carbon source for the fungus. Degradation of chemicals is supported by a carbon source for the fungus but readily available carbon sources such as glucose do not support sustained rates of degradation. Sustained rates were obtained with complex carbohydrates including natural sources. Rates of degradation increased with respect to the concentration of chemical. Degradation of mixtures often proceded faster than the rate of degradation of pure chemicals. For example, the mineralization of pure 2,4,5,2',4',5'-hexachlorobiphenyl proceded much slower (1.1% in 30 days) than did the mineralization of Aroclor 1254 and 1242 (14.3% and 20.3%, respectively, in 30 days). Two percent of pure ^{14}C-naphthalene was mineralized in 30 days but 32% was mineralized when the ^{14}C-naphthalene was present in coal tar contaminated soil. Toxicity of chemicals to the fungus was rare but could be circumvented. The fungus would grow in the presence of used motor oil or coal tar contaminated soil. The toxicity of the fungicide pentachlorophenol (PCP) was reduced by starting with mature mycelia instead of fungal spores. Under these conditions, the fungus continued to mineralize substantial amounts of PCP at concentrations up to 100 ppm. For example, when the initial concentration of PCP was 100 ppm, greater than 20% of the PCP initially present was mineralized in 30 days. Furthermore, disappearance studies showed that approximately 95% of the PCP initially present had been metabolized.

INTRODUCTION

The wood rotting fungus Phanerochaete chrysosporium is a member of the Basidiomycotina. Recent studies in our laboratory (2-9) and by others (1,11,12, 20) have shown that under nutrient nitrogen limiting conditions, this microorganism is able to degrade a wide variety of structurally diverse and environmentally persistent organopollutants to carbon dioxide. The ability to degrade such a wide variety of chemicals has been found to be due, at least in part, to the lignin degrading system of this funugs (1-9,11,12,20).

Lignin is a complex heteropolymer and is possibly the most difficult-to-degrade, naturally occurring organic compound (10). When nutrient nitrogen is depleted in cultures of P. chrysosporium, this fungus secretes a family of peroxidases that are able to catalyze the oxidative depolymerization of lignin as well as a number of other reactions which occur during the biodegradation of lignin (21,22). The peroxidases, which are commonly referred to as ligninases, are also able to catalyze the initial oxidation of many hard-to-degrade organopollutants (5,12,13,20). This is of great significance because the initial oxidation of a chemical is often the most difficult step in its biodegradation.

Because of its broad biodegradative abilities, we have proposed that it may be possible to develop waste treatment systems based on the use of this microorganism in axenic culture or in conjunction with other microorganisms (2). Also, the use of ligninases as additives may prove to be a viable option in some waste treatment processes.

Although the use of P. chrysosporium in the treatment of organochemical wastes holds great potential, in practice there are a number of factors which must be addressed before this microorganism or its extracellular ligninases can be used in such systems. The present study addresses some of these concerns.

METHODS AND MATERIALS

Fungi

Phanerochaete chrysosporium (BKM-F-1767) was obtained from the United States Department of Agriculture, Forest Products Laboratory (Madison, WI). This fungus was maintained on malt agar slant cultures and was stored at room temperature until used. Subcultures were made routinely every 30-60 days.

Radiochemicals

Carbon-14 labeled Aroclor 1242 (33 mCi/mmol), Aroclor 1254 (32 mCi/mmol) and DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) (75 mCi/mmol) were obtained from the Amersham Co. (Arlington Heights, IL) while carbon-14 labeled PCP (pentachlorophenol) (10.57 mCi/mmol), DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethene), 2,4,5,2',4',5'-HCB (2,4,5,2',4',5'-hexachlorobiphenyl (13.09 mCi/mmol) and glucose (1.88 mCi/mmol) were obtained from Pathfinder Laboratories Inc. (St. Louis, MO). Carbon-14 labeled dicofol (2,2,2,-trichloro-1,1-bis(4-chlorophenyl)ethanol) (9.78 mCi/mmol) was a gift from the Rohm and Haas Co. (Springhouse, PA). The purity of radiolabeled chemicals was monitored via thin layer chromatography (TLC) or by high performance liquid chromatography (HPLC) using solvent systems recommended by the vendors. When necessary, these compounds were repurified by TLC. The purity of radiolabeled compounds used in these experiments was 98% or greater. For the special case of the polychlorinated biphenyl mixtures (Aroclor 1254 and Aroclor 1242), the radiolabeled mixtures were compared with authentic unlabeled Aroclor 1242 and Aroclor 1254 by gas liquid chromatography. These studies showed that, although some differences were apparent, the radiolabeled Aroclors appeared to be very similar to their unlabeled counterparts.

Culture Conditions and Mineralization Studies

For most experiments, P. chrysosporium was incubated at 37°-39°C in 10 ml of nutrient nitrogen deficient culture medium as described by Kirk et al. (16). This medium consists of 56 mM glucose, 1.2 mM ammonium tartrate, trace elements and thiamine (1 mg/L) in 20 mM dimethylsuccinate buffer, pH 4.2. Cultures were established by inoculating this medium with spores as described (16). In most experiments, ^{14}C-labeled chemicals, in a minimal volume of acetone, were added at this time. During the first three days of incubation, cultures were grown under ambient atmosphere in 250 ml Wheaton Bottles equipped with a gas exchange manifold. After three days and at three day intervals thereafter, cultures were flushed with oxygen. The atmosphere from each culture was forced through 10 ml of an ethanolamine containing scintillation cocktail which served as a carbon dioxide trap. Carbon-14 labeled carbon dioxide was quantitated by liquid scintillation spectrometry. Details of this mineralization assay have been previously described (2,16).

High Performance Liquid Chromatography

The amount of PCP remaining following its incubation in ligninolytic cultures of P. chrysosporium was determined using a Beckman HPLC system equipped with an Alltech R-Sil C-18 reverse phase column (4.6 x 250 mm). Isocratic elution was performed using acetonitrile:H_2O:glacial acetic acid (75:25:0.125) at a flow rate of 2 ml/min. Elution of PCP was monitored at 238 nm. Quantitation of PCP was accomplished using a Hewlett-Packard model 3390A integrator.

In a typical experiment, a culture that had been incubated with 1 or 100 ppm of PCP was poured into a 30 ml tissue grinder. The culture bottle was then rinsed with 5 ml of ethanol and then with 5 ml of water. Both the ethanol and water rinses were added to the tissue grinder. The fungal mats were then homogenized with five strokes using a motor driven teflon pestle and the final volume was measured. One ml of NaCl saturated water was mixed with each aliquot prior to extraction with hexane. When the initial concentration of PCP in culture was 1 ppm, 4-5 ml of homogenate was extracted with 1 ml of hexane by mixing on a vortex for 30 s. The aqueous and organic phases were then separated by centrifugation. Typically, 50-100 ul aliquots of hexane were used for PCP determinations. Cultures in which the initial concentration of PCP was 100 ppm were extracted in a similar manner except that 0.5 ml of homogenate was extracted with 2 ml of hexane.

RESULTS AND DISCUSSION

Biodegradative Abilities of P. chrysosporium

The development of waste treatment systems based on the use of P. chrysosporium is an attractive concept for many reasons. For example, a wide variety of structurally diverse organopollutants, including some of the most recalcitrant environmental pollutants known, are degraded to carbon dioxide (i.e., mineralized) by this fungus (1-9,11,12,20). The fact that these compounds are degraded to carbon dioxide is an important concept because it demonstrates that a metabolic pathway exists for the complete biodegradation of each of these compounds. It also implies that intermediates formed during biodegradation of the parent compound are also metabolized. It is critical that this occur because metabolites of some organopollutants may be as toxic, or even more toxic than the parent compound. They may also be as difficult to degrade. Table 1 shows that dicofol (2,2,2-trichloro 1,1-bis(4-chlorophenyl)ethanol) a metabolite formed by P. chrysosporium during DDT degradation is itself readily mineralized. Table 1 also demonstrates that DDE is mineralized by this fungus. Although DDE is not a substantial DDT metabolite in this system, it is a major bacterial (17) and mammalian (19) metabolite of DDT. It may also be formed from DDT in the environment and it is at least as toxic and as environmentally persistent as DDT (15,17, 18). Also sites contaminated with DDT would be expected to be contaminated with DDE, especially when these sites have been contaminated with technical preparations of DDT which contain substantial amounts of DDE initially.

The observation that metabolites of organopollutants are themselves metabolized in consistent with the report by Sanglard et al. (20) in which it was shown that water soluble metabolites of benzo(a)pyrene were formed following the formation of organic soluble metabolites in nutrient nitrogen deficient cultures of this fungus. The organic soluble benzo(a)pyrene metabolites were subsequently identified as the benzo(a)pyrene 1,6-, 3,6- and 3,12-quinones (12). It is interesting to note that, unlike the reaction products of the cytochrome P-450 monooxygenases of mammalian systems, the highly carcinogenic 7,8 -diol- 9,10-epoxide of benzo(a)pyrene was not reported to be a benzo(a)pyrene metabolite in this fungus. Hammel et al. (13) have also presented data which indicate that the mutagenic intermediates of pyrene (pyrene-1,6-dione and pyrene-1,8-dione) are also further metabolized by P. chrysosporium. It is also important to note that mutagenic or otherwise toxic metabolites formed by the ligninases of P. chrysosporium would be formed extracellularly thus limiting their interaction with intracellular components such as DNA.

Enhancement of Biodegradation by P. chrysosporium

The initial report (2) from our laboratory was designed to show that a number of environmentally persistent organohalides, as well as the polycyclic aromatic hydrocarbon, benzo(a)pyrene, could be degraded by P. chrysosporium in nutrient nitrogen deficient cultures. Although mineralization did occur, the rate of mineralization in some cases was relatively slow. For example, only 9.3% of the ^{14}C-benzo(a)pyrene initially present was mineralized during 30 days of incubation. Because of the desirability of developing systems which rapidly degrade organopollutants, we have initiated studies which focus on ways to increase the rate of biodegradation of organopollutants using this microorganism. However, it should be

TABLE 1. MINERALIZATION OF DDE AND DICOFOL BY P. CHRYSOSPORIUM[a]

	Initial Concentration (nmoles/culture)	Amount Mineralized[b] (pmoles/culture)	% Mineralized[b]
DDE	15.0	714 ± 180	4.8 ± 1.2
Dicofol	5.0	800 ± 232	16.0 ± 4.6

a. Each culture was grown in 10 ml of the nutrient nitrogen limiting media described by Kirk *et al*. (17).

b. These values represent the amount or percent of ^{14}C-labeled substrate that was converted to $^{14}CO_2$ in 30 days (mean $\pm$ standard deviation, N = 4).

noted that if waste treatment systems can be developed which produce sustained levels of biodegradation at the low rates already demonstrated, even these systems would be sufficient to ensure the timely destruction of these chemicals.

Efforts to increase the rate of biodegradation of organopollutants by *P. chrysosporium* have employed a number of strategies. For example, we have shown that increasing the concentration of growth substrate (glucose) from 26 mM to 112 mM resulted in a 2.5 fold increase in the amount of ^{14}C-DDT mineralized during a 30 day incubation period (3). An interesting facet of these studies is the fact that the initial rate of mineralization (i.e. the rate observed between day 3 and day 18) was the same for all of the glucose concentrations studied. The difference in the amount of ^{14}C-DDT mineralized was due to the fact that, in cultures containing low (28 mM and 56 mM) glucose concentrations, the rate of mineralization rapidly declined after 18 days of incubation whereas this decline was not as pronounced in cultures containing higher concentrations of glucose. These results suggest that the ability to mineralize organopollutants is dependent upon the availability of a carbon source such as glucose which can serve as a growth substrate. This hypothesis was confirmed in studies in which supplemental glucose was shown to increase the rate and extent of ^{14}C-DDT mineralization when added to cultures in which the glucose concentration had been depleted (2,3).

The ability of supplemental glucose to increase the rate and extent of biodegradation may be due to at least two phenomena. First, the addition of supplemental glucose may simply increase the overall rate of fungal metabolism and, as a consequence, organopollutants or their metabolites are mineralized at a faster rate. Secondly, since hydrogen peroxide is a required cosubstrate for the ligninases which are responsible for the initial oxidation of many organopollutants, it is possible that the addition of supplemental glucose allows the fungus to produce the required hydrogen peroxide as a co-product of the glucose oxidase system.

The suitability of using more complex carbohydrates to support growth and mineralization of organopollutants has also been studied. Figure 1 demonstrates that 1% cellulose and 1% starch are both substantially better than 1% glucose in supporting mineralization of ^{14}C-DDT. Possibly the most important aspect of this experiment is the fact that, although the initial rate of mineralization with all three substrates was nearly identical, the rate of mineralization when starch or cellulose served as growth substrate did not decline as rapidly as when glucose was used. Furthermore, in the cultures containing cellulose or starch, substantial amounts of ^{14}C-DDT continued to be mineralized for the duration of the 90 day incubation period.

In addition to cellulose and starch, a number of inexpensive and readily available cellulosic materials were tested for their ability to support growth and

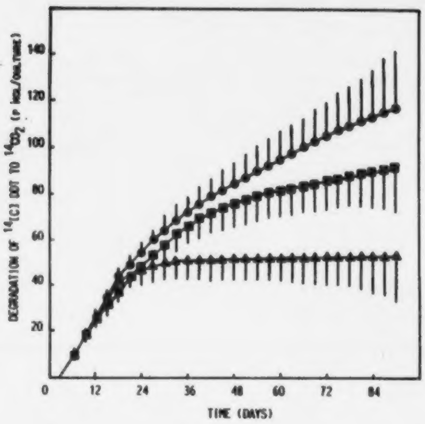

Figure 1. Mineralization of ^{14}C-DDT by *P. chrysosporium* using 1% starch (closed squares), cellulose (closed circles) or glucose (closed triangles) as growth substrate. The initial concentration of ^{14}C-DDT was 365 pmoles/culture.

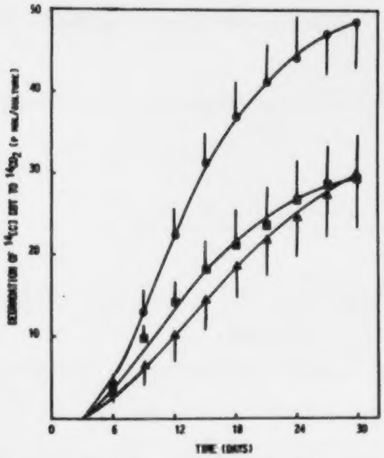

Figure 2. Mineralization of ^{14}C-DDT by *P. chrysosporium* grown on 5% wheat straw (closed circles), newspaper (closed squares) or corn cobs (closed triangles). The initial concentration of ^{14}C-DDT was 365 pmoles/culture.

^{14}C-DDT mineralization. Figure 2 shows that 5% (w/v) wheat straw, used newspaper and corn cobs all support growth of the fungus and mineralization of ^{14}C-DDT. Although these materials were less efficient that starch or cellulose in the support of ^{14}C-DDT mineralization, they did support substantial amounts of mineralization (13.2% ± 5.8, 8.1% ± 5.0, and 8.2% ± 3.3, respectively). This, coupled with the fact these materials are inexpensive and readily available suggests that they may be suitable for use as growth substrates in a practical waste treatment system.

Biodegradation of Complex Mixtures

The lignin (and organopollutant) degrading system of *P. chrysosporium* is relatively non-specific and non-stereoselective. This property is very important because, unlike other microorganisms, one would expect that this fungus might be able to degrade complex mixtures of xenobiotics. Indeed, Table 2 demonstrates that ^{14}C-Aroclor 1254 (a mixture of tetra-, penta- and hexa-chlorobiphenyls) and ^{14}C-Aroclor 1242 (a mixture of mono-, di-, tri- and tetra-chlorobiphenyls) undergo substantial mineralization in nutrient nitrogen deficient cultures of *P. chrysosporium*. These studies are in good agreement with the work of Eaton (11) who first showed that ^{14}C-Aroclor 1254 was degraded by *P. chrysosporium*. It is interesting to note that mineralization of the Aroclor mixtures proceeded more rapidly than mineralization of pure ^{14}C-2,4,5,2',4',5'-hexachlorobiphenyl. The reason for this is, at present, unknown. It may be that this highly chlorinated biphenyl congener is simply more resistent to degradation than other congeners in these PCB mixtures. On the other hand, it is interesting to speculate that certain individual components of complex mixtures may exert synergistic effects on the oxidative biodegradation of other components in the mixture. There is precedent for such interactions. For example, addition of veratryl alcohol has been shown to increase the rate and extent of degradation of benzo(a)pyrene (12) and 4-methoxymandelic acid (4). We have observed a similar phenomena. Carbon-14 labeled naphthalene is mineralized slowly (2%/30 days) in nutrient nitrogen deficient cultures of *P. chrysosporium*. However, when ^{14}C-naphthalene was added to cultures containing coal tar contaminated soil, Tween 20 and veratryl alcohol, 32% of the ^{14}C-naphthalene was mineralized during the same incubation period (Bumpus and Aust, unpublished observation).

TABLE 2. MINERALIZATION OF BIPHENYL AND POLYCHLORINATED BIPHENYLS BY P. CHRYSOSPORIUM[a]

	Initial Concentration (nmoles/culture)	Amount Mineralized[b] (pmoles/culture)	% Mineralized[b]
Biphenyl	1.25	367 ± 91	29.4 ± 7.3
Aroclor 1242	1.25	254 ± 19	20.3 ± 0.2
Aroclor 1254	1.25	179 ± 47	14.3 ± 3.8
2,4,5,2',4',5'-HCB[c]	5.0	57 ± 20	1.1 ± 0.4

a. Culture conditions were the same as described in Table 1.

b. These values represent the amount or percent of ^{14}C-labeled substrate that was converted to $^{14}CO_2$ in 30 days (mean ± S.D., N = 4 for Biphenyl, Aroclor 1254 and 2,4,5,2',4',5'-HCB, N = 3 for Aroclor 1242).

c. Because of the low amounts of 2,4,5,2',4',5'-HCB that were mineralized, this experiment was continued for a total of 115 days. At the end of this extended incubation period 126.0 ± 32.0 pmoles (2.5 ± 0.6%) of the 2,4,5,2',4',5'-HCB initially present had been mineralized. During this period, supplemental glucose (56 mM) was added at 30 day intervals.

Toxicity Problem

A prerequisite for any microorganism used in waste treatment systems is the ability to survive in the presence of the organopollutants that it is intended to degrade. Our toxicity studies have focused of the ability of P. chrysosporium to mineralize the fungicide, pentachlorophenol. We have shown that, like a number of other organopollutants, ^{14}C-PCP mineralization is promoted in nutrient nitrogen deficient cultures of P. chrysosporium whereas mineralization is suppressed in nutrient nitrogen sufficient cultures, thus suggesting that mineralization is due, at least in part, to the lignin degrading system of this funugs (9). Furthermore, our studies demonstrated that the initial rate and the extent of mineralization increased with respect to ^{14}C-PCP concentration over the range of 16.6 ppb to 333 ppb (Bumpus and Aust, unpublished observation). Attempts to study ^{14}C-PCP mineralization at higher concentrations (i.e. in the parts per million range) were hindered because PCP concentrations higher than 4 ppm were lethal to the fungus when cultures were intiated with spores. The problem of lethality was circumvented by allowing cultures of P. chrysosporium to grow for six days before adding PCP. In these studies (Table 3), in which toxicity was measured by the ability of PCP to inhibit respiration (i.e. conversion of ^{14}C-glucose to $^{14}CO_2$), it was shown that although PCP concentrations between 10 and 100 ppm caused substantial inhibition of respiration, they were not lethal to the fungus. And, significantly, substantial amounts of ^{14}C-PCP were still degraded as shown in disappearance and mineralization studies.

In other studies we have shown that this microorganism was able to survive in the presence of a number of relatively adverse conditions. For example, we have shown this fungus was able to grow in the presence of high concentrations (300 ppm) of DDT, used motor oil (20% w/w) and coal tar contaminated soils.

Taken together, these results suggest that conditons may be developed which will allow this fungus to grow and degrade organopollutants in a number of potentially toxic environments. The suitability of using this microorganism in a given situation will, of course, require individualized study of the site in question.

TABLE 3. Mineralization and Disappearance of PCP by *P. chrysosporium*[a]

Initial Concentration of PCP		Amount Mineralized	% Mineralized	% Disappearance
nmoles/culture	ppm	nmoles/culture		
37.5	1	18.8 ± 1.9	50.1 ± 5.1	100[c]
375.0	10[b]	158 ± 45	42.1 ± 12.0	N.D.[d]
3750.0	100[b]	841 ± 615	22.4 ± 16.4	95

a. Each culture (10 ml) was allowed to grow for 6 days at which time PCP was added in a minimal volume of acetone (< 20 µl). Other culture conditions were the same as those described in Table 1. Cultures were incubated for 30 days.

b. PCP caused 57.1 ± 37% and 74.3 ± 12.5% inhibition of the initial rate of respiration in cultures containing 10 and 100 ppm PCP, respectively. Respiration was measured as the amount of $^{14}CO_2$ evolved from ^{14}C-glucose per day.

c. Detection limit = 50 ppb

d. Not determined.

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GROWTH OF THE WHITE-ROT FUNGUS *PHANEROCHAETE CHRYSOSPORIUM* IN SOIL

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ABSTRACT

Phanerochaete chrysosporium is a white-rot fungus with a demonstrated ability to degrade chlorinated organics in pure liquid culture to carbon dioxide. This ability suggests that the fungus may have potential as an *in situ* hazardous waste degrader. However, no data exist regarding the ability of *P. chrysosporium* to survive and grow in soil. That information is required for an effective evaluation of the ability of the fungus to degrade organo-pollutants *in situ*. The objective of this study was to investigate the influence of soil biotic and abiotic factors on survival and growth of the organism. This paper will summarize our research results to date on the effects of soil type, temperature, water potential and acidity on growth of the fungus in sterile soils.

INTRODUCTION

The fungus *Phanerochaete chrysosporium* Burds. (Burdsall and Eslyn 1974) (Basidiomycotina, Corticiaceae), has been shown to oxidize several halogenated aromatic pollutants to carbon dioxide and has been proposed as an agent for biological treatment of recalcitrant organo-halides (Eaton 1985; Bumpus *et al.* 1985; Huynh *et al.* 1985). On-site processing or *in situ* hazardous waste treatment methods that employ *P. chrysosporium* will require application of the fungus to soil for treatment of contaminants. *Phanerochaete chrysosporium* is a white-rot wood decay fungus that is often found in wood chip storage piles (Burdsall and Eslyn 1974). Its growth in soils has not been reported. Therefore, the ability of the fungus to grow in soils, as well as abiotic and biotic soil factors affecting fungal survival, growth and degradative ability must be determined before the possibility of developing a biological treatment method can be evaluated.

The investigations reported in this paper were designed to assess the effects of various soil types, water potentials and temperatures on growth of *P. chrysosporium* in sterile soils. Hazardous waste sites occur on a great variety of soil types. Soil water potential and temperature are major factors influencing both fungal growth and decomposition processes (Cooke and Rayner 1984). These parameters were chosen for the initial studies described here, because an assessment of their influence should yield information critical to future investigations into the degradative ability of *P. chrysosporium* in soil, and ultimately to the development of a biological treatment method.

Materials and Methods

Inoculum Preparation

Phanerochaete chrysosporium Burds. (BKM F-1767; ATCC no. 24725) was maintained at room temperature (25°C) on 2% malt agar slants (Kirk *et al.* 1978). Soil inoculum consisted of aspen (*Populus tremuloides* Michx.) pulpwood chips (1.5 x 0.5 x 0.25 cm^3) thoroughly grown through with *P. chrysosporium*. Chips were inoculated with mycelial suspensions of the fungus as follows: The fungus was cultured in 125-ml Erlenmeyer flasks containing 10 ml of basal medium (Kirk *et al.* 1978). Inoculum for these starter cultures consisted of conidial suspensions taken from two-week-old slants (Kirk *et al.* 1978). After incubating at 39°C for 1.5 d in Erlenmeyer flasks, mycelial mats were collected, washed with sterile deionized distilled water and fragmented in a blender. The resulting slurry was resuspended in the volume of sterile deionized distilled water needed to adjust the moisture content of the aspen chips to 60% (dry weight basis). Aspen chips had been sterilized by autoclaving in aluminum foil-covered 2-L Erlenmeyer flasks at 121°C and 103.5 kPa for 1 h. Mycelia were added to sterile chips at a rate of 0.02% mycelia:chips (w/w, dry weight basis). Inoculated chips were incubated at 39°C for approximately 3 wk.

Soils

Soil samples from the A horizons of Marsham sandy loam (Fine-silty, mixed, mesic, Mollic-Hapludalf), Xurich sandy loam (Fine-silty over sandy, mixed, mesic, Typic-Haplaquoll) and the B2t horizon of Batavia silty clay loam (Fine-silty, mixed, mesic, Typic-Hapludalf) were used in the present study. Soils were air-dried, passed through a 2 mm sieve and stored in 4-mil plastic bags at 4°C. Samples of each soil were analyzed for physical and chemical properties by Dr. M. F. Jurgensen of the Michigan Technological University, School of Forestry and Wood Products, Houghton, Michigan. These soils were chosen to represent ranges of texture, acidity and organic matter and nutrient contents. Results of soil chemical analyses are presented in Table 1.

Experimental Design

An experiment designed to test the influence of soil type, water potential and temperature on growth of *P. chrysosporium* in sterile soils consisted of a 3 x 3 x 3 factorial in a completely randomized design; the experiment was repeated once.

Moisture content of each soil was adjusted to levels corresponding to soil water potentials of -0.03, -0.15 and -1.5 MPa. Petri plates (20 x 90mm diam.) were filled with soil; within a soil type, an equal weight of soil on a dry weight basis was added to each plate. The weight of each filled plate was recorded and soils and plates sterilized by autoclaving for 0.5 h at 121°C and 103.5 kPa. Autoclaving was performed on each of three consecutive days to assure sterility; no contamination problems were encountered.

Soils were inoculated by aseptically placing an inoculum chip into the soil in the center of a plate. Controls were prepared by inoculating plates with inoculum chips which had been re-sterilized by autoclaving for 1 h at 121°C and 103.5 kPa. Plates were then placed in incubators held at 25°, 30° and 39°C. Soil water potentials were maintained daily by weighing each plate and adjusting, if necessary, with the appropriate amount of sterile deionized distilled water. Each run of the experiment was 2 weeks in duration.

In a separate experiment the effect of acidity on growth of *P. chrysosporium* in the Batavia soil was investigated. Appropriate amounts of $CaCO_3$ were added to Batavia soil to raise the pH 1 and 2 pH units above the original (pH 4.8). Studies showed that 1 g of $CaCO_3$ per kg of Batavia soil and a 2-week incubation period were required to raise the pH value of the soil 1 unit. After autoclaving, pH values were 4.8, 5.8 and 6.8. Soil water potential was adjusted to -0.03 MPa. Sterilization and inoculation procedures were as previously described. The experiment was 2 weeks long.

Growth Assessment

At the end of 2 wk, growth of *P. chrysosporium* was assessed using a qualitative rating system. This system was based on a visual assessment of the amount of growth by the fungus over the soil surface. The rating system was as follows:

Growth rating-description

0-no growth of fungus from chip into soil
1-some hyphae growing from chip into soil
2-some scattered hyphal growth in the vicinity of the chip plus some conidiation
3-medium coverage of soil surface by hyphae plus conidiation
4-medium-dense coverage of soil surface plus dense conidiation
5-dense coverage of soil surface plus dense conidiation

A rank transformation approach was used to analyze the data. The entire set of observations (*i.e.* growth ratings) were ranked, with the smallest observation having rank 1, the second smallest rank 2, and so on. Average ranks were assigned ties (Conover and Iman 1981). The transformed data were subjected to analysis of variance and reported as ranks of the growth assessment data. Soil type means were compared using Tukey's HSD method. All other treatment means were compared using single degree of freedom contrasts (Chew 1977).

Results and Discussion

Soil Type

Soil type greatly influenced growth of *P. chrysosporium* ($p = .0001$). Growth of the fungus was greatest in the Marsham, intermediate in the Xurich and least in the Batavia soil (Table 2). It is interesting to consider which factor(s) were responsible for the growth differences of *P. chrysosporium* among the three soils.

Soil acidity is one possibility. Cooke and Rayner

Table 1. Selected soil chemical properties of the three studied soils.

Soil type	CEC[1]	BS%	Acidity[2]		OM%	N%[3]	Ca	Mg	K	P	B	Mn	Zn	S
			B	A			ppm							
			pH											
Batavia	22.9	29.5	5.06	4.65	0.5	0.05	1950	850	145	75	0.6	12.5	1.9	9.7
Marsham	50.7	66.4	7.13	6.59	12.0	0.46	4900	1650	90	17	1.3	9.0	12.2	11.3
Xurich	16.5	24.0	7.74	7.12	39.0	0.18	1675	640	80	17	0.8	77.5	6.4	3.9

[1] Determined using the Ammonium Acetate Method (Thomas 1982)

[2] B= before autoclaving; A= after autoclaving

[3] Determined using the Kjeldahl prodedure for Total N (Bremmer and Mulvaney 1982)

Table 2. Mean growth ranking of *Phanerochaete chrysosporium* in three soils.

Soil Type	Growth Ranking
Batavia	27c*
Marsham	80a
Xurich	57b

*Means followed by a different letter are significantly different (Tukey's HSD, $\alpha = .05$)

(1984) observed, however, that the influence of soil acidity on fungal growth is difficult to assess because of the ability of fungi to radically alter the pH value of their environment, and because the effects of acidity are modified by so many other environmental factors. It was not surprising, therefore, that growth of *P. chrysosporium* , which has an optimum of pH 5.5 in liquid culture (Kirk *et al.* 1978), was greater in the neutral to slightly acid Marsham and Xurich soils than in the strongly acid Batavia soil. If acidity were responsible for the poor growth in the Batavia soil, reducing soil acidity should have been beneficial. However, this was not the case ($p = .4523$). The failure of decreasing soil acidity in the Batavia soil to benefit fungal growth, and the observation that optimum growth was found in the slightly acid (*i.e.* pH 6.59) Marsham soil when the optimum for *P. chrysosporium* in liquid culture is pH 5.5, suggests that soil acidity does not play a significant role in mediating the growth of this fungus in soil. Evidently this organism, too, alters the pH value in the vicinity of its hyphae to create a favorable environment.

A second factor likely to influence growth is soil organic matter. The three studied soils differed greatly in this respect (Table 1). The ability of *P. chrysosporium* to assimilate the organic matter in the three soils is unknown. Given the magnitude of the differences, if organic matter content were the primary factor in controlling growth of *P. chrysosporium* , greatest growth would have been expected in the Xurich soil. Because this was not the case (Table 2), some factor other than organic matter content was controlling growth.

A third factor likely to influence growth is soil nitrogen content. In natural environments, this is the nutrient which is most likely to be in such a limited supply as to affect mycelial growth (Cooke and Rayner 1984). Nitrogen content varied greatly between the three soils studied. Regression of fungal growth on soil nitrogen content revealed a strong positive relationship ($R^2 = .924$) (Figure 1). The strength of this relationship suggests that soil nitrogen content played a significant role in mediating growth of *P. chrysosporium* .

Growth habit of the fungus was also affected by soil type. In the Marsham and Xurich soils, hyphae were observed to be growing primarily across the soil surface, although at the highest levels of growth it was evident from observing the bottom of the plates that the fungus had penetrated through the soil. In the Ba-

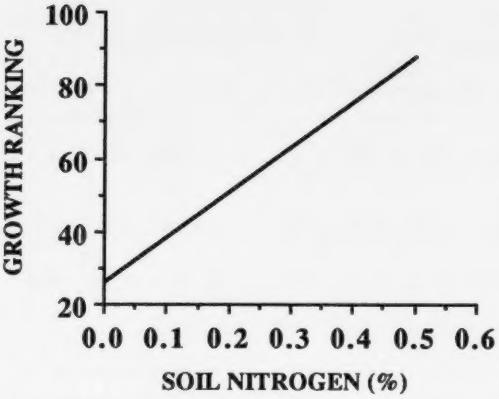

Figure 1. Regression of growth ranking on soil nitrogen content for *Phanerochaete chrysosporium* grown in three soils (y = 123.6x + 26.1, $R^2 = .924$).

tavia soil, hyphae were not observed growing across the soil surface, but appeared to grow through the soil, surfacing at various locations.

There was evidence for an interaction between soil type and experimental run (p = .0003). This interaction was probably the result of better growth in the Marsham and Xurich soils in Run 2 than in Run 1 (Figure 2). During Run 1, relative humidity in the incubators was maintained at levels which resulted in appreciable daily soil moisture losses, particularly at 39 °C. During the second run, humidity levels in the incubators were increased and soil moisture losses greatly reduced. *Phanerochaete chrysosporium* might have been able to benefit from the increased incubator humidity levels during Run 2 by obtaining moisture directly from the atmosphere, or loss of hyphal vigor due to partial desiccation could have been prevented. Either might explain the significantly greater growth of the fungus in the Marsham and Xurich soils during Run 2. Because *P. chrysosporium* did not grow on the soil surface in the Batavia soil it would not be expected to benefit as much from an increase in atmospheric moisture. Indeed, growth of the fungus in the Batavia soil during Run 2 was not significantly different from that in Run 1 (Figure 2). In light of the above, the data from each run were analyzed separately to assess the effect of soil water potential on growth of *P. chrysosporium.*

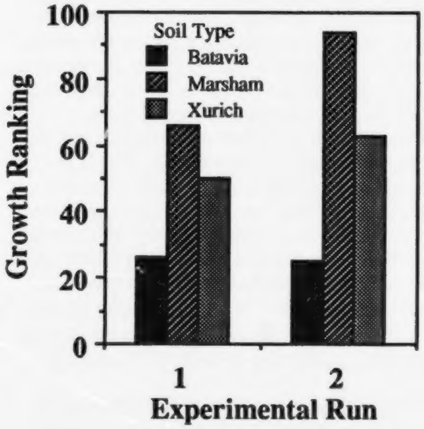

Figure 2. Growth ranking of *Phanerochaete chrysosporium* in three soils by experimental run.

Soil Water Potential

A significant (p = 0.0002) linear relationship between growth of *P. chrysosporium* and soil water potential over all soils was observed in Run 1 (Figure 3). In contrast, soil water potential had less influence on growth in Run 2 (p = .1399). As indicated above, however, the fungus growing in the Marsham and Xurich soils might have benefited from increased levels of atmospheric moisture which effectively masked the influence of soil water potential on growth. In the Batavia soil where surface growth of the fungus was sparse, there was a significant (p = 0.0017) linear relationship between growth of the fungus and soil water potential (Fig. 4).

The linear increase in growth of *P. chrysosporium* in response to increasing water potential over the range

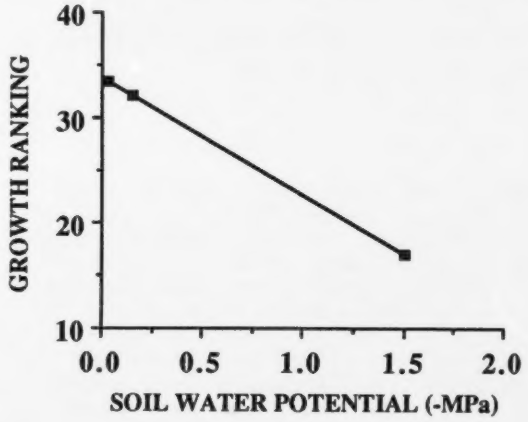

Figure 3. Regression of growth ranking on soil water potential for *Phanerochaete chrysosporium* grown in three soils-Run 1 (y = 1.119x + 33.767, $R^2 = .233$).

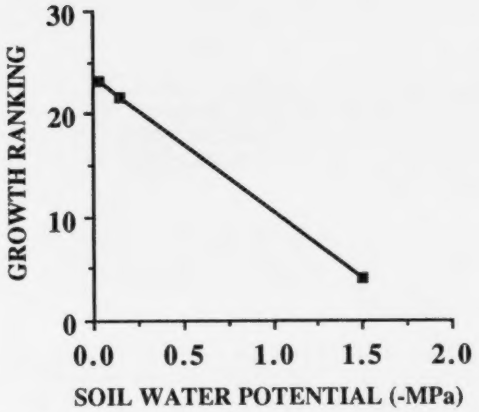

Figure 4. Regression of growth ranking on soil water potential for *Phanerochaete chrysosporium* grown in the Batavia soil-Run 2 ($y = 1.299x + 23.551$, $R^2 = .47$)

-1.5 to -0.03 MPa is consistent with what other workers have observed for both wood decay and soil fungi in general. Griffin (1977) proposed that growth of wood decay fungi occurs at a decreasing rate from 0 to -4.0 MPa, and presented data indicating that maximum growth of five wood decay basidiomycetes occurred at -0.15 MPa osmotic potential. Wood decay fungi have been placed in a group of organisms, which includes some soil basidiomycetes and gram-negative bacteria, that is extremely sensitive to water potential, with an optimum growth response *ca.* -0.1 MPa osmotic potential, and little growth below -2.0 MPa (Griffin 1981). The optimum soil water potential range for microbial growth and metabolic activity is generally considered to be between -0.01 and -0.03 MPa (Sommers *et al.* 1981). The soil water potential growth optimum for *P. chrysosporium* might be greater than -0.03 MPa.

Sommers *et al.* (1981) suggested that water potential influences decomposition of soil organic materials in a 2-phase process whereby an initial rapid decrease in decomposition in the -0.03 to -1.5 MPa matric potential range is followed by a second phase in which decomposition decreases linearly with decreasing water potential. Therefore, soil water potential optima for growth of, and degradative activity by, *P. chrysosporium* may be very similar.

Temperature

Evidence was obtained for better growth of *P. chrysosporium* at 30° and 39°C compared to growth of the fungus at 25°C (Table 3). The magnitude of this difference appeared to be directly related to the relative growth among soil types. Most soil fungi are mesophiles with temperature optima between 25° and 35°C, but with an ability to grow from *ca* 15° to 45°C (Cooke and Rayner 1984). *Phanerochaete chrysosporium* is also mesophilic and has a temperature optimum of *ca.* 39°C on 2% malt agar (Burdsall and Eslyn 1974). Ability of the fungus to grow as well at 30°C as it did at 39°C was not expected. It is possible that at 39°C some other factor (*e.g.* nutrient availability or water stress) offsets the benefits of the more optimal temperature. However, *P. chrysosporium* did not appear to exploit the total soil volume in any of the plates, indicating that nutrient pools were also not fully exploited. Studies are underway to determine the minimum temperature at which *P. chrysosporium* will grow in the soil.

Table 3. Effect of soil temperature on growth ranking of *Phanerochaete chrysosporium* in three soils.

	Soil Temperature (°C)			
Soil	39°	30°	25°	P*
Batavia	28	31	21	.1198
Marsham	86	89	66	.0170
Xurich	64	59	47	.0531

* Probability of a larger F value for the single degree of freedom contrast of growth at 30° and 39°C versus growth at 25°C.

Conclusions

All parameters investigated, except acidity, influenced growth of *P. chrysosporium* in the three soil types. Soil type had a significant effect on growth and growth habit. Nitrogen content appeared to play a major role in mediating growth of the fungus in the soils, and could well have been responsible for the differences in fungal growth among the soil types. Future studies to elucidate the extent to which available nitrogen influences growth of *P. chrysosporium* in soil are warranted. Increasing soil water potential from -1.5 MPa to -0.03 MPa resulted in greatly increased growth of *P. chrysosporium* . The data indicate that growth of the fungus might benefit from soil water potentials above -0.03 MPa. Growth of the fungus was significantly greater at 30° and 39°C than at 25°C.

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BIOLOGICAL TREATMENT OF SELECTED AQUEOUS ORGANIC HAZARDOUS WASTES

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ABSTRACT

This paper describes tests performed in order to evaluate the fate of aqueous organic hazardous waste compounds in the activated sludge process. Gas, liquid and waste solids samples were taken from acclimated activated sludge systems to determine amounts that were volatilized, biodegraded and associated with the wasted solids. Results discussed here include two compounds, methyl ethyl ketone and 1,1,1 trichloroethane.

INTRODUCTION

With the reauthorization of RCRA and the concurrent restrictions on land disposal of hazardous wastes, the EPA is assessing waste treatment techniques that can be substitutes for, or precursors to, land disposal. Concentrations of hazardous, organic compounds in aqueous, RCRA listed wastes must be greatly reduced in order to achieve levels acceptable for land disposal. For this type of waste in concentrations up to 10,000 ppm, the activated sludge process is a potentially applicable treatment process. However, a lack of data on the treatment of solvents at high concentrations exists.

To fulfill this need, two bench-scale activated sludge systems were constructed. The systems were operated at a theoretical 10-day solids retention time (SRT) with a 24-hour hydraulic retention time (HRT). Each system was fed a synthetic wastewater spiked with the test compound. Compounds tested in this study were methyl ethyl ketone (MEK) and 1,1,1 trichloroethane (TCA). Each compound was tested at two concentrations.

The purpose of this program was to study the changes in fate of selected organic priority pollutants in continuous bench-scale activated sludge systems over a broad concentration range. This information will be helpful in determining whether or not this treatment process introduces toxic compounds to the atmosphere, concentrates them in the wasted sludge, or destroys them via biodegradation.

MATERIALS & METHODS

Two completely mixed, continuous flow, bench-scale activated sludge systems were utilized. Each system consisted of a pyrex glass column 15.2 cm in diameter and 91.4 cm in height. The total liquid volume was 11 liters with a depth of 58.4 cm. This allows for an air volume above the liquid level of 5.7 liters. A metal plate with inlet and outlet holes covers the top of the reactor. Ports are located along the side of the reactor for inlet/outlet lines. An airstone located just above the bottom of the reactor diffuses air into the system for mixing and aerating purposes. Air flow rate and pressure were monitored. Air flow rates varied between approximately

800 ml/min to 1800 ml/min depending on the dissolved oxygen (D.O.) concentration and mixed liquor solids concentration of the reactor.

The primary and secondary clarifiers were also made of pyrex glass and were the same size. A glass dome, with inlet and outlet ports for air venting and sampling purposes, covered each clarifier. Each had a liquid volume of 1.5 liters with an air head space volume of 0.8 liters. Liquid flowed by gravity in sequence from the primary clarifier to the reactor and on to the secondary clarifier. A recycle pump connected to a timer was used to periodically transfer the settled secondary solids back to the reactor. Solids were wasted directly from the reactor by a pump connected to a timer. Synthetic feed was peristaltically pumped from a refrigerated stock solution to the primary clarifier. The organic spike compound was introduced to the feed lines by means of a syringe pump. A static, in-line mixer was used immediately in front of the primary clarifier to blend the spike with the feed. Off-gases from the reactor and clarifiers were vented.

The activated sludge systems were used to treat a synthetic wastewater consisting of a "base mix" plus the selected priority pollutant of interest. The synthetic feed was prepared daily and stored at 4°C. The base mix constituents are listed in Table 1.

Table 1

Synthetic Feed Constituents

Ethylene glycol	Phenol
Ethyl alcohol	Ammonium sulfate
Acetic acid	Magnesium sulfate
Phosphoric acid	Manganese sulfate
Glutamic acid	Calcium chloride
Glucose	Ferric chloride

The base mix was diluted so that the wastewater exerted a 5-day Soluble Biochemical Oxygen Demand ($SBOD_5$) of approximately 500 mg/l, with an average Soluble Organic Carbon (SOC) of 420 mg/l. This synthetic wastewater is the formula used by Kincannon, et. al. (1983) in studying priority pollutants in activated sludge treatment systems. A synthetic feed was chosen over an industrial or municipal wastewater for two basic reasons: A synthetic feed is more consistent in terms of $SBOD_5$ and SOC concentrations than an industrial or municipal wastewater; and secondly, it facilitates comparisons between spiked compounds.

Much of the existing data on the fate of compounds in activated sludge are at concentrations up to 200 mg/l (e.g. Kincannon et. al., 1983). Based on this, initial concentrations not exceeding 200 mg/l were chosen. The first measured concentrations tested were 55 mg/l for MEK and 141 mg/l for TCA. The second concentrations tested were 430 mg/l for MEK and 174 mg/l for TCA. The addition of MEK increased the influent $SBOD_5$ to 620 mg/l and 1340 mg/l for each concentration respectively. The addition of TCA had a negligible affect on the influent $SBOD_5$ at either concentration.

Return activated sludge, for the purpose of initial seeding, was obtained from a large-scale system at the EPA Test and Evaluation (T&E) Facility. A 100 ml sample of primary effluent from the same large-scale system was added daily to each systems' reactor throughout the study. This was done to provide a continued supply of organisms found in wastewater that are not available in a synthetic feed. The two individual systems were acclimated to the synthetic wastewater for at least one month before the spike was introduced. Both systems were allowed to acclimate to the first spike concentration for at least a month. A theoretical solids retention time (SRT) of 10 days was targeted, controlled by wasting 10% of the reactor volume over a 24 hour period. Average SRT's were about 7 days for both systems, due to a loss of solids in the effluent. The hydraulic retention time (HRT) was 24 hours. Routine process performance monitoring measurements and their respective frequencies are listed in Table 2.

When the systems assumed steady state conditions following acclimation to the spike compound, a two-week sampling period ensued. During the sampling period, samples for gas chromatograph analyses were taken three times a week for the two weeks. Samples taken during this period consisted of 24 hour composite liquid influent and effluent samples (pumped to teflon bags to minimize volatilization), a 24-hour composite wasted mixed liquor sample, a grab primary effluent liquid sample and grab off-gas samples from the primary and

Table 2 Routine Process Monitoring

Measurement	Frequency	Method
$SBOD_5$	3 x per wk	EPA 405.1*
SOC	5 x per wk	EPA 415.2*
TSS/VSS	1 x per day	EPA 160.1*
D.O.	6 x per day	EPA 360.1*
D.O. Uptake Rate	1 x per day	Std. Meth. 213A

* USEPA (1983)

secondary clarifiers, as well as the reactor. All liquid composite samples were kept at 4°C. Liquid samples were transferred to clean amber glass bottles with Teflon caps, sealed with no headspace.

Off-gases were sampled using 0.63 cm O.D. borosilicate glass sorbent tubes containing 0.25 g Tenax. Two tubes were used in series for each sample. Air sampling pumps were used to provide a constant air flow rate, which was further controlled by needle valves and measured by rotameters. Purified air at atmospheric pressure was used to replace the off-gas removed from the clarifiers.

Methyl ethyl ketone measurements were obtained by EPA Method 8015 (SW-846, 3rd ed., 1986). EPA Method 601 for Purgeable Halocarbons was used to measure 1,1,1 trichloroethane (Federal Register, 40 CFR Part 136, Part VIII, 10/26/84).

Table 3

Process Monitoring Data for MEK System
(all values in mg/l)

	MEK Concentration 55 mg/l				MEK Concentration 430 mg/l			
	Before Testing		During Testing		Before Testing		During Testing	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
MLVSS	779	121	1093	336	2430	298	2189	182
EFF. VSS	101	62	44	22	55	30	84	57
EFFL. $SBOD_5$	---	---	16	8	33	56	23	19
EFFL. SOC	38	21	17	6	10	6	4	4

Table 4

Process Monitoring Data for TCA System
(all values in mg/l)

	TCA Concentration 141 mg/l				TCA Concentration 174 mg/l			
	Before Testing		During Testing		Before Testing		During Testing	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
MLVSS	958	129	1335	178	682	221	467	29
EFFL. VSS	134	112	91	65	327	58	345	75
EFFL. $SBOD_5$	17	16	63	53	6	4	10	3
EFFL. SOC	20	12	27	14	13	8	8	1

RESULTS

Two organic compounds, each at two concentrations, have been studied in the completely-mixed, continuous flow, activated sludge systems. Table 3 and Table 4 summarize basic process monitoring data used to assess the systems' performance. Mean values with standard deviations for a two-week period prior to testing, and during the test period itself, are presented. All test period values are 14-day means, except TCA concentration #2, which is a 3-day mean. Because a five-week period separated sample days two and three thru seven for the first MEK concentration, the data for the two weeks prior to testing are prior to the last five sample days.

For the first concentration of each compound seven data points were collected. For the second concentration, six data points for MEK and three data points for TCA were collected. The average mass fluxes with the mean percentages of the influent mass distributed to each fraction, as calculated from an average mass balance around the primary clarifier and both the reactor and secondary clarifier, are shown in Tables 5 and 6. Data from the second TCA concentration were excluded since this concentration was inhibitory to the system.

Table 5

Fates of MEK in Activated Sludge

	MEK Concentration 55 mg/l		MEK Concentration 430 mg/l	
	Flux (mg/min)	Percent	Flux (mg/min)	Percent
	PRIMARY MASS BALANCE			
Influent	0.418		3.269	
Primary Effluent	0.404	96.7	3.358	102.7
Primary Volatilization	0.046	11.0	0.084	2.6
Unknown Primary Loss (+)/Gain (-)	-0.030	-7.7	-0.170	-5.2
	SECONDARY MASS BALANCE			
Reactor Influent	0.404		3.358	
Apparent Biodegradation	0.382	94.6	3.012	89.7
Reactor Stripping	0.012	3.0	0.342	10.2
Secondary Volatilization	0.0002	0.1	0.003	0.1
Waste Sludge	0.0004	0.1	0.000	0.0
Effluent	0.009	2.3	0.001	0.0

Table 6

Fates of TCA in Activated Sludge

	TCA Concentration 141 mg/l Flux (mg/min)	Percent
	PRIMARY MASS BALANCE	
Influent	1.072	
Primary Effluent	0.741	69.0
Primary Volatilization	0.221	20.6
Unknown Primary Loss(+)/Gain(-)	0.110	10.4
	SECONDARY MASS BALANCE	
Reactor Influent	0.741	
Apparent Biodegradation	0.161	21.8
Reactor Stripping	0.565	76.2
Secondary Volatilization	0.004	0.5
Waste Sludge	0.001	0.1
Effluent	0.010	1.4

Table 7

Removal Efficiencies of Organic Pollutants

Compound	Influent (mg/l)		Effluent (mg/l)		Percent Overall Removal
	Mean	Std. Dev.	Mean	Std. Dev.	
Methyl ethyl ketone	55	9	0.5	1.2	>99
	430	59	0.9	0.3	>99
1,1,1 Trichloroethane	141	37	3.8	6.5	97
	174	32	3.5	0.3	98

DISCUSSION

Table 7 summarizes the overall organic pollutant removal efficiencies of both systems at each concentration. It is seen that greater than 89% of the MEK was biodegraded at both concentrations. The large increase in MLVSS concentrations after the increase in MEK concentration from 55 mg/l to 430 mg/l would seem to support the notion that MEK is very easily biodegraded.

Operating the activated sludge system while it was spiked with MEK was somewhat difficult. The floc formed in the system was fine and light, hence, not settling well. Bridging at the bottom of the secondary clarifier developed, having the effect of lowering the concentration of solids in the return activated sludge (RAS). Therefore, solids were washed out of the system in the secondary effluent. As the MEK concentration increased, secondary effluent solids concentration increased as more solids were being formed in the reactor, compounding the settling problems.

Another factor influencing the performance of the MEK system may have been nutrient deficiency. As the concentration of MEK was increased, the influent $SBOD_5$ increased, but the base mix remained constant. This resulted in a decrease of the ratio of nutrients to $SBOD_5$. The poor floc formation observed at the higher MEK concentration may have been partially caused by this deficiency.

As is shown in Table 6, most of the TCA was removed via stripping in the reactor. This is to be expected since TCA is highly volatile. Primary volatilization and biodegradation also accounted for significant percentages of the overall removal.

As with MEK, poor system operation occurred when spiked with TCA. For each concentration tested, TCA seemed inhibitory to biological growth. This is evident by the fact that initial acclimation took four months; one month at 10 mg/l and three months at 141 mg/l. Effluent solids concentrations at 141 mg/l TCA averaged approximately 100 mg/l VSS. The solids were fine and light and did not settle well. When the influent concentration was further increased to a measured concentration of 174 mg/l, the system exhibited signs of shock and inhibition. The primary clarifier contents, usually cloudy, turned crystal clear. Little growth occurred in the reactor. Solids did not settle in the secondary clarifier. Effluent solids concentrations were almost the same as MLVSS concentrations as shown in Table 4.

One major problem encountered when working with TCA was in uniformly dispersing it into the feed solution. For the first test phase, an amount equal to 295 mg/l was injected into the feed line, yet only 141 mg/l was measured in the feed. For the second test concentration, an amount equal to 705 mg/l was injected, whereby only 174 mg/l was measured in the feed, and 251 mg/l measured in the primary effluent. Many factors may account for this inconsistency including: the density of TCA (1.339 g/cc), low solubility in water, volatility, as well as inadequate sampling techniques. Thus, effects on the system may have been caused by concentrations of TCA higher than reported.

SUMMARY

This study has shown that methyl ethyl ketone and 1,1,1 trichloroethane can be removed by the activated sludge process, but both chemicals at the concentrations tested are disruptive to the basic operation of the unmodified process. For MEK, biodegradation was the most important removal mechanism, while most TCA was removed via stripping.

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ASSESSMENT OF ALTERNATIVE TECHNOLOGIES FOR TREATING SPENT ELECTROPLATING SOLUTIONS AND SLUDGES

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ABSTRACT

Off-site commercial hazardous waste treatment facilities were evaluated to generate support data for the Environmental Protection Agency's land disposal ban. Establishing treatment standards for electroplating wastewater and sludges is a high priority task with respect to the land disposal ban. One facility treated electroplating solutions with cyanide oxidation, hexavalent chromium reduction, a combination of lime and sulfide precipitation, and vacuum filtration. Electroplating sludges were stabilized with calcium hypochlorite, ferric sulfate or lime. Of particular interest is the use of waste streams as treatment reagents. This report summarizes data used to evaluate these treatment technologies for electroplating solutions and sludges.

INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 mandate that a ban on the land disposal of hazardous wastes be implemented. EPA will choose the "best demonstrated available technology" (BDAT) for each waste category banned and will determine treatment performance levels for each waste category based on the BDAT. Hazardous constituents of treated wastes must be reduced below specified levels. To meet the provisions of the land disposal ban, EPA has prioritized waste categories to be addressed. Electroplating wastes and other wastes containing metals and cyanide are a high priority.

In support of the efforts of the Office of Solid Waste (OSW) to implement the provisions of the RCRA land disposal ban, the Hazardous Waste Engineering Research Laboratory (HWERL) has initiated several programs to evaluate alternatives to land disposal. A major component of these programs has been the field evaluation of existing full-scale commercial treatment facilities.

FACILITY DESCRIPTION

One facility evaluated under this program treated wastes generated by the electroplating industry, as well as other metal finishing operations. The facility treats liquid wastes by the following unit operations: cyanide oxidation, hexavalent chromium reduction, metals precipitation and vacuum filtration. Total treatment capacity for liquid wastes is ten million gallons per year. Solid wastes contaminated with cyanide, hexavalent chromium, and various metals are stabilized with calcium hypochlorite, ferric sulfate crystals, and lime, respectively. This process is designed to delist the solid wastes. The facility operates 24 hours per day for six days a week.

PROCESS DESCRIPTIONS - LIQUID WASTE

Incoming Waste

Liquid waste streams, defined as having less than 20 weight percent total suspended solids, are screened to confirm their manifest composition. A treatment simulation is conducted to determine the required amount of treatment reagents. Wastes are segregated by type: acid, neutral, alkali, cyanide content, and hexavalent chromium content. If a waste contains greater than 1 part per million (ppm) of cyanide, it is segregated for pretreatment. Wastes containing greater than 25,000 ppm of cyanide are not accepted. As many as five separate sources may be incorporated into one batch for treatment.

Cyanide Oxidation

Cyanide wastes are treated by alkaline chlorination. A lime slurry is used for pH adjustment to 10 and a waste sodium hypochlorite solution is used as the oxidizing agent. The cyanide is oxidized to cyanate in a single-stage batch reaction. The amount of hypochlorite added to each batch is predetermined by the plant chemist and controlled by the operator. The level of excess hypochlorite is monitored every 15 minutes by an operator using potassium iodide starch test paper. Additional hypochlorite is added, if needed, to maintain an excess concentration of at least 100 ppm. One hour after the initial hypochlorite addition a filtered sample is analyzed for amenable cyanide. Treatment continues until cyanide is not detectable in a filtered sample. The cyanide reaction is optimum at a pH of 11 to 12. Since cyanide forms strong complexes with ferrous iron, it is important to oxidize the cyanide before reducing hexavalent chromium. Further treatment of the waste is conducted in the same reactor tank.

Hexavalent Chromium Reduction

Hexavalent chromium is reduced to trivalent chromium in a single-stage batch reaction, using waste iron acid as the reducing agent. The treatment tank is first charged with lime slurry to minimize corrosion of the stainless steel mixing system. Enough lime slurry is added to neutralize all waste acids that would be treated for hexavalent chromium reduction and subsequent metals precipitation. Maintaining an alkaline mixture also helps to eliminate emissions of by-product gases (e.g. NO_2, Cl_2). The stoichiometric weight ratio of iron acid to hexavalent chromium is 3.2 to 1. A 10 percent excess of iron is maintained to ensure complete reduction. Temperature and pH are monitored periodically throughout the reaction. Treatment is continued until a spot test shows no detectable hexavalent chromium. Additional treatment is conducted in the same reactor vessel.

Metals Precipitation

Metals are first precipitated with a lime slurry. A predetermined volume of lime slurry is used which includes 200 to 300 gallons in excess of the required volume. At the optimum pH range of 8 to 10, metal cations will precipitate as insoluble hydroxides. The process is dependent on the solubilities of the metal hydroxides, which are a function of pH and water quality. Because each metal hydroxide has a minimum solubility at a different pH, it is difficult to obtain high removal efficiencies for every metal. An agitator keeps the suspended floc in suspension. After ten minutes of agitation the pH is checked. When the pH does not change with time, the reaction with lime is complete.

Because of stringent discharge limits, precipitation with a waste sulfide stream is used as a polishing step to remove the remaining dissolved metals. In general, metal sulfides have lower solubilities than metal hydroxides at the same pH. After sulfide addition, a filtered sample is analyzed for chromium, copper, nickel and zinc. The sample filter cake is subjected to an abbreviated EP Toxicity test. The facility has determined that if a waste can pass their abbreviated test, it will also pass the 24-hour test. When the sample results are acceptable, the contents of the tank are pumped to a precoat vacuum filter.

Vacuum Filtration

The treated wastewater is subjected to vacuum filtration to separate liquids and solids. Perlite, a volcanic ash, is currently used as a precoat although diatomaceous earth has been used in the past. The dewatered solids fall onto a solids conveying system and are stored in a bulk container. A sample is subjected to the 24 hour EP toxicity test to ensure the waste is nonhazardous.

Ultimate Disposal

The dewatered sludge is sent to the facility's lined, nonhazardous landfill. The filtrate is discharged to the local publicly owned treatment works (POTW). The facility continuously monitors the sewer discharge to assure compliance with local standards. The liquid waste treatment process is illustrated in Figure 1.

Air Emissions

The facility uses a two-stage scrubber to capture fumes from the treatment tanks, caustic storage and sulfide storage tanks.

A one-stage scrubber is used to capture fumes released from the acid storage tanks. Both scrubbers have an induced flow of 1000 standard cubic feet per minute (scfm). The pH in each scrubber is maintained between 12 and 14 by the addition of sodium hydroxide. The overflow spillage from each scrubber is collected in its respective sump and pumped to a treatment tank when the sump is full.

PROCESS DESCRIPTION - SOLID WASTE

Incoming Waste

Prior to being unloaded at the treatment facility, each load of solid waste is weighed and tested to verify its contents. A treatment simulation is conducted on a sample to determine the required amounts of treatment chemicals and to make sure the waste can pass the EP Toxicity test. Incoming loads are segregated on the basis of their water content.

Treatment

The solids handling/treatment process is designed to delist solids that may be contaminated with cyanide, hexavalent chromium, and/or various other metals. The untreated solids are lifted by an overhead traveling crane into a mix chamber that is agitated by a modified pugmill operation. After mixing, bags of reagents are manually added into the mix cell. Calcium

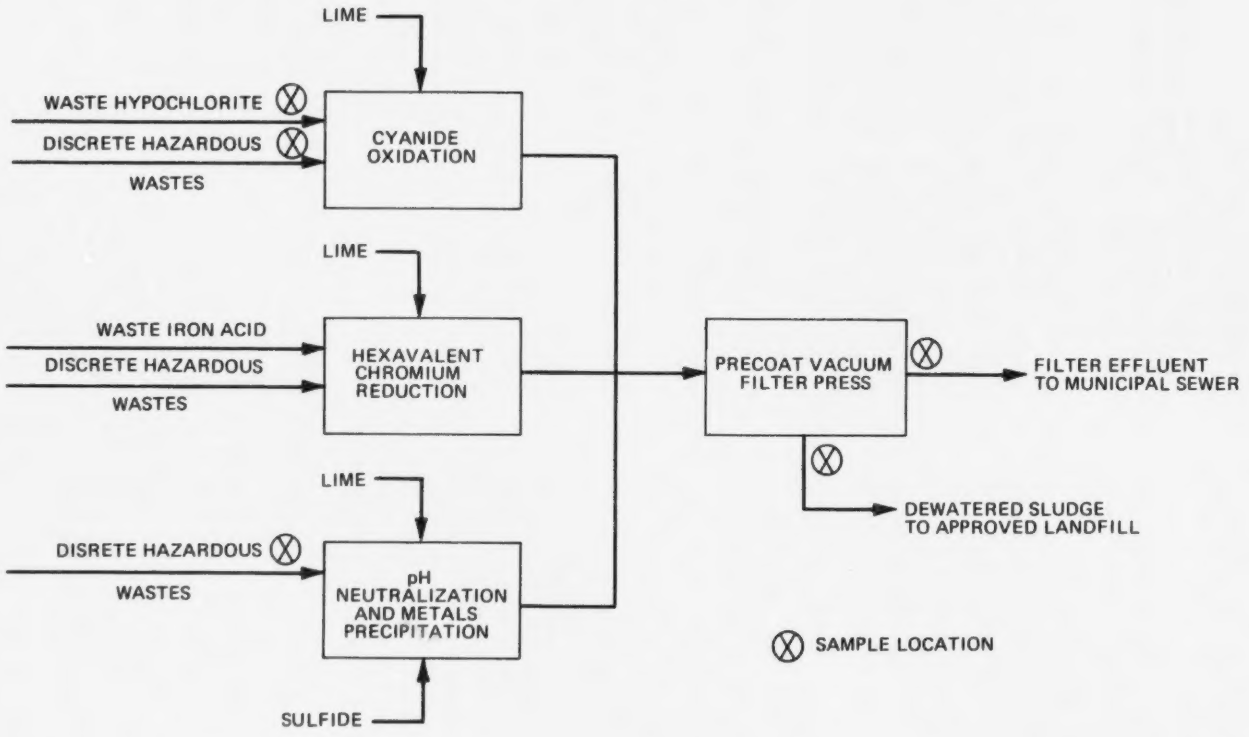
LIME
WASTE HYPOCHLORITE ⊗
DISCRETE HAZARDOUS ⊗
WASTES
CYANIDE OXIDATION
LIME
WASTE IRON ACID
DISCRETE HAZARDOUS
WASTES
HEXAVALENT CHROMIUM REDUCTION
LIME
DISRETE HAZARDOUS ⊗
WASTES
pH NEUTRALIZATION AND METALS PRECIPITATION
SULFIDE
PRECOAT VACUUM FILTER PRESS
⊗
FILTER EFFLUENT TO MUNICIPAL SEWER
⊗
DEWATERED SLUDGE TO APPROVED LANDFILL
⊗ SAMPLE LOCATION

FIGURE 1. LIQUID WASTE TREATMENT PROCESS

hypochlorite, ferric sulfate crystals and lime are added for sludges contaminated with cyanide, hexavalent chromium and various metals, respectively. Water is also added if the mix is too dry. After thirty minutes of treatment, the mix cell contents are dropped into a roll-off container. All treated solids are then subjected to the 24 hour EP Toxicity test to confirm they have been rendered nonhazardous. Figure 2 depicts the solids handling treatment operation.

Ultimate Disposal

The delisted sludge is disposed of in the facility's lined, nonhazardous landfill.

SAMPLING RESULTS

The objective of this sampling program was to provide HWERL with information on existing hazardous waste treatment technologies which provide alternatives to land disposal. Specific objectives included the following:

- identify industries whose wastes are treated by alternative technologies.
- determine treatment capacity, waste acceptance criteria and other pertinent information about each facility.
- evaluate the effectiveness of each unit operation.
- discuss environmental impacts of alternative technologies (e.g. air emissions, sludge disposal, effluent discharge).

Fourteen complete batches of waste were processed during the sampling episode, including eleven liquid and three solid batches. Of the eleven batches of liquid waste, three required pretreatment for cyanide oxidation, six required hexavalent chromium reduction and all eleven were treated by chemical precipitation and vacuum filtration.

Liquid Waste Treatment System

Influent Wastes. Discrete wastes treated during the sampling episode were primarily from fabricated metal products industries. Each batch treated contained an average of 46 percent by volume electroplating waste. Table 1 summarizes the types of waste streams including their SIC code and RCRA waste code.

These discrete waste streams have widely varying concentrations of metals. The wastes had high concentrations of solids, ranging from 4,500 to 259,200 ppm. Ninety six percent of the solids were dissolved. The pH ranged from 1 to 13. In the three batches pretreated by cyanide oxidation, the total cyanide concentration in discrete wastes averaged 7.6 ppm. Free cyanide was present at less than 0.10 ppm.

The most concentrated waste was a chromic acid plating bath solution with a pH of 1, containing the following metals: antimony (68 ppm), hexavalent chromium (78,400 ppm), total chromium (103,800 ppm), copper (3,500 ppm), lead (60 ppm), nickel (40 ppm) and zinc (100 ppm).

Treatment Tank Composite. As many as five discrete wastes were composited for batch treatment. Treatment tank composite samples were analyzed for volatile organics, total organic halide (TOX) and total organic carbon (TOC), in addition to

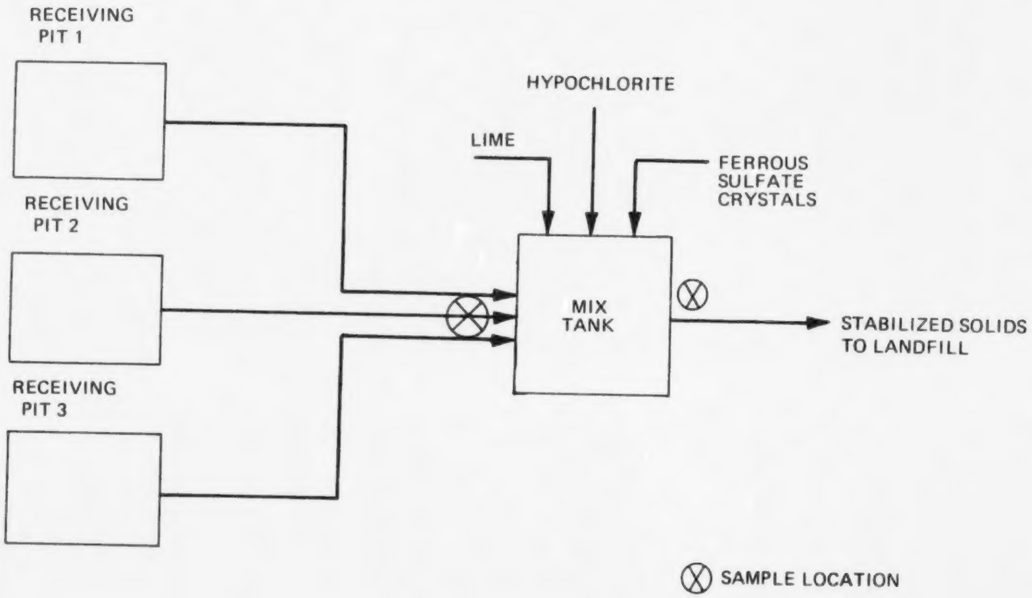
RECEIVING PIT 1
RECEIVING PIT 2
RECEIVING PIT 3
LIME
HYPOCHLORITE
FERROUS SULFATE CRYSTALS
MIX TANK
STABILIZED SOLIDS TO LANDFILL
SAMPLE LOCATION

FIGURE 2. SOLIDS TREATMENT PROCESS

TABLE 1. INDUSTRIAL SOURCES OF LIQUID WASTES

Industry Category	Industry (SIC Code)	Process	RCRA waste code
Fabricated metal products	Refurbishing of used field artillery (3471)	Chrome & brass electroplating	F006
Fabricated metal products	Electroplating (3471)	Chrome electroplating	D002
Fabricated metal products	Manufacture of toasters, toaster ovens, and coffee makers (3634)	Nickel and chrome electroplating	F006
Fabricated metal products	Reclamation of tin from scrap metal (3341)	Etching, electroplating	D002
Chemical manufacturing and processing	Manufacture of glass perfume bottles (3621)	Etching	D002
Fabricated metal products	Manufacture of aluminum windows, doors, sashes and mouldings (3442)	Conversion coating of aluminum	F019
Fabricated metal products	Manufacture of semiconductors and electrical connectors (3678, 3643)	Nickel, chrome and gold electroplating	F006
Fabricated metal products	Manufacture of aluminum bottle caps (3466)	Cleaning	D002
Fabricated metal products	Surface finishing of sheet steel-anodizing, painting and etching (3316)	Cleaning	K062

D002 - Corrosive waste that has a pH less than or equal to 2 or greater than or equal to 12.5.

F006 - Wastewater treatment sludges from electroplating operations except from the following processes: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc - aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.

F019 - Wastewater treatment sludges from the chemical conversion coating of aluminum.

K062 - Spent pickle liquor from steel finishing operations.

toxic metals and other parameters. Toluene, 1,1-dichloroethane, ethylbenzene and 1,1,1 trichloroethane were detected in several treatment tank composite samples at levels below 300 ppb. The pH ranged from 7 to 10. TOX varied from 0.00 to 0.36 percent with a mean of 0.11 percent. TOC varied from 0 to 5,900 ppm with a mean of 1,821 ppm. Total and free cyanide were not detected above the analytical detection limit of 2 ppm.

Waste Treatment Chemicals. Waste streams were used as treatment reagents for cyanide oxidation, hexavalent chromium reduction and sulfide precipitation.

A waste hypochlorite stream is used as the oxidizing agent in cyanide treatment. The waste used during the sampling episode was a by-product scrubber solution from the production of chlorinated chemicals (RCRA Waste Code D003). Analytical data showed low concentrations of barium (43 ppm) and zinc (4 ppm). The total solids content ranged from 250,000 ppm to 330,000 ppm with the majority of solids being dissolved. The pH of the wastestream was 13.

A waste iron-bearing stream is used to reduce hexavalent chromium. The waste used during the sampling episode was a waste pickling acid from the metal processing industry (RCRA Waste Code K062). The following metals were detected in this waste stream: arsenic (3 ppm), total chromium (3500 ppm), copper (532 ppm), nickel (1553 ppm), and zinc (7 ppm). The total solids content ranged from 70,700 ppm to 148,600 ppm with the majority of solids being dissolved. The pH of the wastestream was 1.

A waste stream containing sulfide is used in a polishing step following precipitation with lime. In all batches the waste stream was a by-product scrubber solution from the production of a sulfurized ester (RCRA Waste Code D003). Insignificant concentrations of total chromium, lead and zinc were detected in this waste stream. The total solids content was 94,000 ppm with most solids being dissolved. The pH of the wastestream was 13.

Vacuum Filter Effluent. Soluble metals data for the vacuum filter effluent were consistently below detection limits. This indicates that the precipitation process was effective in removing soluble metals. Total metals data for the filtrate were comparable to the soluble metals data, which indicates insignificant levels of insoluble metals. The filtration system was effective in removing insoluble metal hydroxides and metal sulfides.

Metal removal efficiencies by precipitation and filtration are summarized in Table 2. The removal efficiency for hexavalent chromium is a result of chromium reduction as well as precipitation and filtration. Metals not listed in Table 2 were not detected during the sampling episode.

In Table 3, data for the vacuum filter effluent are compared to the facility's discharge limits. Analytical detection limits for mercury and cyanide were higher than the discharge limits. The hexavalent chromium concentration exceeded the discharge limit three times for waste treated by chromium reduction and once for waste treated only by precipitation and filtration. The zinc concentration exceeded the discharge limit once during the sampling episode. All

TABLE 2. METAL REMOVAL EFFICIENCY

Metal	Percent Removal Range
Chromium, Total	99.97 - 100.00
Chromium, Hexavalent	99.98 - 100.00
Copper	99.78 - 100.00
Lead (3 batches only)	99.94 - 100.00
Nickel	99.90 - 100.00
Zinc	70.88 - 99.93

TABLE 3. COMPARISON OF FACILITY DISCHARGE TO CITY DISCHARGE LIMITS

Pollutant	Vacuum Filter Effluent (ppm, range)	Discharge Limit (ppm)
Toxic Metals:		
Chromium (total)	0.10 - 0.20	0.6
Chromium (hexavalent)	0.011 - 0.190	0.05
Copper	0.07 - 0.21	0.8
Lead	<0.01 - 0.01	0.5
Mercury	<0.1	0.003
Nickel	0.31 - 0.40	1.0
Silver	<0.2	1.0
Zinc	0.06 - 1.62	1.0
Other Parameters:		
Cyanide	<2	0.15
pH	7 - 10	5.5 - 10.5

NS = Not Sampled

other parameters listed in Table 3 were detected below the discharge limits.

The vacuum filter effluent samples contained an average solids content of 5.2 weight percent with 90 percent of the solids being dissolved. Volatile organic compounds were not present above analytical detection limits.

Vacuum Filter Cake. The filter cake samples were dry with a solids content of 35 weight percent. All samples passed the paint filter test. The total organic carbon content averaged 0.57 percent. Alkalinity was 220,000 mg/l as $CaCO_3$. The filter cake samples were subject to the EP toxicity and the recently promulgated Toxicity Characteristic Leaching Procedure (TCLP) test. Table 4 summarizes the analytical results and the EPA treatment standards. All metals were found at levels below the regulatory limits. Volatile organic compounds were detected in TCLP extracts at levels below regulatory limits.

Solid Waste Treatment System

Influent Wastes. Discrete solid wastes treated during the sampling episode were primarily from fabricated metal products industries. Table 5 summarizes the types of waste streams, including their SIC code and RCRA waste code. All waste streams were dewatered residuals from one or more of the following treatment processes: cyanide oxidation, hexavalent chromium reduction and lime neutralization. Discrete wastes were composited prior to sampling.

The untreated solids composite had a solids content of 41 weight percent and a total organic carbon content of 0.48 percent. All samples passed the paint filter test. Acidity ranged from 0 to 1,400 mg/l as $CaCO_3$ and alkalinity ranged from 0 to 35,000 mg/l as $CaCO_3$. The metals content was highly variable. Total chromium, lead, nickel and zinc were detected at levels ranging from 100 ppm to 7,000 ppm. Barium, cadmium, hexavalent chromium and copper were detected at levels below 100 ppm. Low concentrations of volatile organic compounds were present.

Stabilized Solids. Metals results for stabilized solids are summarized in Table 6. All metals were found at levels below the regulatory limits in the sample extracts. Styrene (200 ppb) and total xylenes (78 ppb) were detected as well as other volatile organics (<30 ppb). Volatile organics in TCLP extracts were detected at levels below the regulatory limits. The stabilized solids had a solids content of 46 weight percent and a total organic carbon content of 0.57 percent. All stabilized solids samples passed the paint filter test. Alkalinity averaged 135,000 mg/l as $CaCO_3$.

CONCLUSION

The facility discussed in this paper was successful in treating electroplating and other metal finishing waste. The cyanide oxidation operation could not be evaluated due to high analytical detection limits. Metal removal efficiency was consistently higher than 99.8 percent except for one batch where zinc removal was 70.9 percent. In most cases, the facility's effluent was acceptable with respect to discharge limits. Hexavalent chromium and zinc exceeded discharge limits at least once during the sampling episode.

The filter cake from liquid waste treatment and stablilized solids can be delisted and disposed of in a nonhazardous landfill. Toxic metal and volatile organic analyses of TCLP extracts showed compliance with regulatory limits. In general, the facility was well maintained with proper attention to controlling air emissions, to monitoring effluent quality and to producing non-hazardous solids.

TABLE 4. METALS RESULTS FOR VACUUM FILTER CAKE

	Compositional (ppm)	EP Toxicity Extract (mg/l)	TCLP Extract (mg/l)	TCLP (a) Regulatory Limit (mg/l)
Antimony	<10	0.01	--	--
Arsenic	5	<0.05	0.016	5.0
Barium	40	0.03	0.28	100.0
Beryllium	<2	0.01	--	--
Cadmium	53	0.031	<0.020	1.0
Chromium (hexavalent)	1.77	<0.005	--	--
Chromium (total)	16,300	<0.01	<0.05	5.0
Copper	775	0.03	--	--
Lead	2,800	0.18	<0.10	5.0
Mercury	<1	<0.002	<0.0002	0.2
Nickel	4,700	0.09	--	--
Selenium	<10	<0.01	<0.040	1.0
Silver	14	0.06	<0.020	5.0
Thallium	<10	0.06	--	--
Zinc	2,100	0.10	--	--

(a) Federal Register, Volume 51, Number 144, June 13, 1986, p. 21675.

TABLE 5. INDUSTRIAL SOURCES OF SOLID WASTES

Industry Category	Industry (SIC Code)	Process	RCRA waste RCRA waste code
Metal processing and refining	Primary iron and steel production (3312)	Pickling	D007
Fabricated metal products	Manufacture of semiconductors (3674)	Etching and nickel electroplating	F006
Fabricated metal products	Manufacture of chains (3471)	Nickel and chrome electroplating	F006
Metal processing and refining	Primary steel production with secondary plating of sheet steel (3312)	Pickling, chrome and zinc electroplating	D007
Electrical and electronic equipment	Secondary battery manufacture (3691)	Lead-acid battery production	D008
Fabricated metal products	Manufacture of motor vehicles and passenger car bodies (3711)	Conversion coating of aluminum	F019
Fabricated metal products	Manufacture of iron pipe fittings (3312)	Cleaning	K062

D007 - A solid waste that exhibits the characteristic of EP toxicity due to the concentration of the toxic contaminant chromium.

D008 - A solid waste that exhibits the characteristics of EP toxicity due to the concentration of the toxic contaminant lead.

F006 - Wastewater treatment sludges from electroplating operations except from the following processes: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc - aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating or carbon steel; and (6) chemical etching and milling of aluminum.

F019 - Wastewater treatment sludges from the chemical conversion coating of aluminum.

K062 - Spent pickle liquor from steel finishing operations.

TABLE 6. METALS RESULTS FOR STABILIZED SOLIDS

Toxic Metal	Compositional (ppm)	EP Toxicity Extract (mg/l)	TCLP Extract (mg/l)	TCLP[a] Regulatory Limit (mg/l)
Antimony	30	<0.01	--	--
Arsenic	5	<0.05	0.015	5.0
Barium	60	0.20	0.19	100.0
Beryllium	<2	<0.01	--	--
Cadmium	21	0.014	<0.05	1.0
Chromium (hexavalent)	0.30	<0.005	--	--
Chromium (total)	7,500	0.04	0.15	5.0
Copper	775	0.11	--	--
Lead	1,500	0.14	<0.10	5.0
Mercury	<1	<0.002	<0.0002	0.2
Nickel	4,900	0.22	--	--
Selenium	<10	<0.01	<0.20	1.0
Silver	8	0.01	<0.02	5.0
Thallium	<10	<0.01	--	--
Zinc	11,000	0.04	--	--

(a) Federal Register, Volume 51, Number 144, June 13, 1986, p. 21675.

SOLVENT RECOVERY TECHNOLOGIES

By

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ABSTRACT

The increasing cost for disposal of hazardous wastes presents a favorable climate for recovery of materials and energy from hazardous wastes. In the case of waste solvents, the land disposal restrictions imposed by EPA on those materials on November 7, 1986, will make disposal much more difficult and costly.

This paper describes approaches to recovery of solvent wastes: fuel blending, distillation, and steam stripping. The technologies are described and data are presented from EPA programs to evaluate these technologies.

INTRODUCTION

Annual waste solvent generation in the U.S. is approximately 3.2 billion gallons (1). Prior to the imposition of the congressionally mandated land disposal restrictions on November 7, 1986, about 1.2 billion gallons of hazardous waste solvents were disposed of to the land, primarily to surface impoundments. About 300 million gallons went to deep well injection and 195 million gallons were incinerated. About 545 million gallons were recycled and the remainder went to storage. Of the amount that was recycled, 80 percent was recycled at the source of generation (onsite) (2).

New regulations promulgated by EPA under the Hazardous and Solid Waste Amendments of 1984 (HSWA) require substantial treatment of the waste prior to land disposal and also put severe limitations on waste storage. HSWA also requires that EPA evaluate deep well injection to determine its suitability for long term waste disposal. It is obvious that acceptable management techniques must be found to accommodate the discrepancy between current waste solvent generation rates and treatment capacity.

Certain conclusions are obvious. First, more solvent wastes will be incinerated. In particular, commercial incineration will increase. Wastes which are burned onsite are most likely burned as fuel in boilers. Waste that will tend to show up at commercial incineration facilities will have low value as fuel.

Second, waste minimization will get increased attention as costs increase and disposal options decrease. Minimization practices will more than likely result in lower volumes of total solvent waste entering the waste management system but these solvent wastes will be more dilute and of lower quality as a fuel, therefore making the wastes less amenable to incineration.

Therefore, there will exist a greater need for application and improvements of concentration techniques. Once the waste solvent is concentrated, it will be a function of purity, degree of separation, and fuel value that determines whether the solvent is reused as a solvent or burned as a fuel.

Solvent Recovery Technologies

Solvent recovery technologies consist of three general types of processes: concentration, refinement, and use as fuel. Examples of concentration processes include drying, evaporation, steam stripping, and simple distillation. The most prominent example of refinement is fractional distillation. Solvents are burned as fuel in industrial boilers and industrial furnaces such as cement kilns, lime kilns, and steel making furnaces. The remainder of this paper will provide descriptions of the principal solvent reclamation processes, including thin film evaporation, steam stripping, and fractional distillation. Data are provided on the performance of these technologies in spent solvent processing operations.

Steam Stripping

Figure 1 illustrates a typical steam stripping process. Waste enters near the top of the column and then flows by gravity countercurrent to steam (3). As the waste passes down through the column it contacts vapors rising from the bottom of the column that contains progressively less volatile organic compounds. The concentration of volatile compounds in the waste reaches a minimum at the bottom of the column where it is discharged. The overhead vapor is condensed as it exits the column and the condensate is then decanted to achieve solvent/water separation. Reflux may or may not be used, depending on the desired composition of the overhead stream.

Steam stripping is most applicable to low concentrations of organic materials in water. Volatile organic concentrations in excess of 10 percent may be more cost effectively treated with distillation. Also, organic compounds with boiling points in excess of 150°C cannot be treated effectively with steam stripping.

Recently, EPA conducted bench scale steam stripping of a petrochemical process wastewater stream containing halogenated organics. The waste stream contained a number of constituents found in waste solvents. Table 1 exhibits data on compound removal efficiency for the 5.08 cm diameter, 367 cm high, counterflow column. Recoveries of volatile organics averaged 85 percent with steam flows of 18 to 24 percent of the feed (4).

The concentrated solvent product from the steam stripper could be used in an application where mixed constituents are acceptable (e.g. certain degreasing operations). It could also be processed further to separate constituents (through distillation) or burned as a fuel.

Thin Film Evaporation

Agitated thin film evaporation (ATFE) is the most effective high volume evaporation technique for separating low and medium boiling point waste components, while concentrating high boiling and/or solid constituents. Its ability to handle a wide range of waste viscosities (1 to 1,000,000 cps) makes it the most common treatment device at large commercial solvent recycling companies.

Liquid waste is fed to the top of ATFEs where longitudinal blades mounted on a motor driver rotor centrifugally force the waste against the heat transfer surface which is the inside wall of the cylindrical vessel. This surface is enclosed in a heating jacket which employs steam or hot oil as the heating medium. Temperatures of the working fluid can reach 650°F. The agitation and liquid film are maintained by the blades as they move along the heat transfer surface. The blade tips typically travel 30 to 40 feet per second at a clearance of 0.007 to 0.10 inches which creates high turbulence. This facilitates efficient heat and mass transfer, shortens required waste residence time and creates a degree of mixing which maintains solvents in a manageable suspension without fouling the heat transfer surface. Viscosity is the critical waste property that affects thin film evaporator performance.

A schematic of an ATFE and associated pretreatment and post-treatment options are shown in Figure 2 (5). The pretreatment techniques most often undergoing ATFE are a previous solvent recovery process, oil or suspended solids removal, or a

FIGURE 1. **STEAM STRIPPING PROCESS**

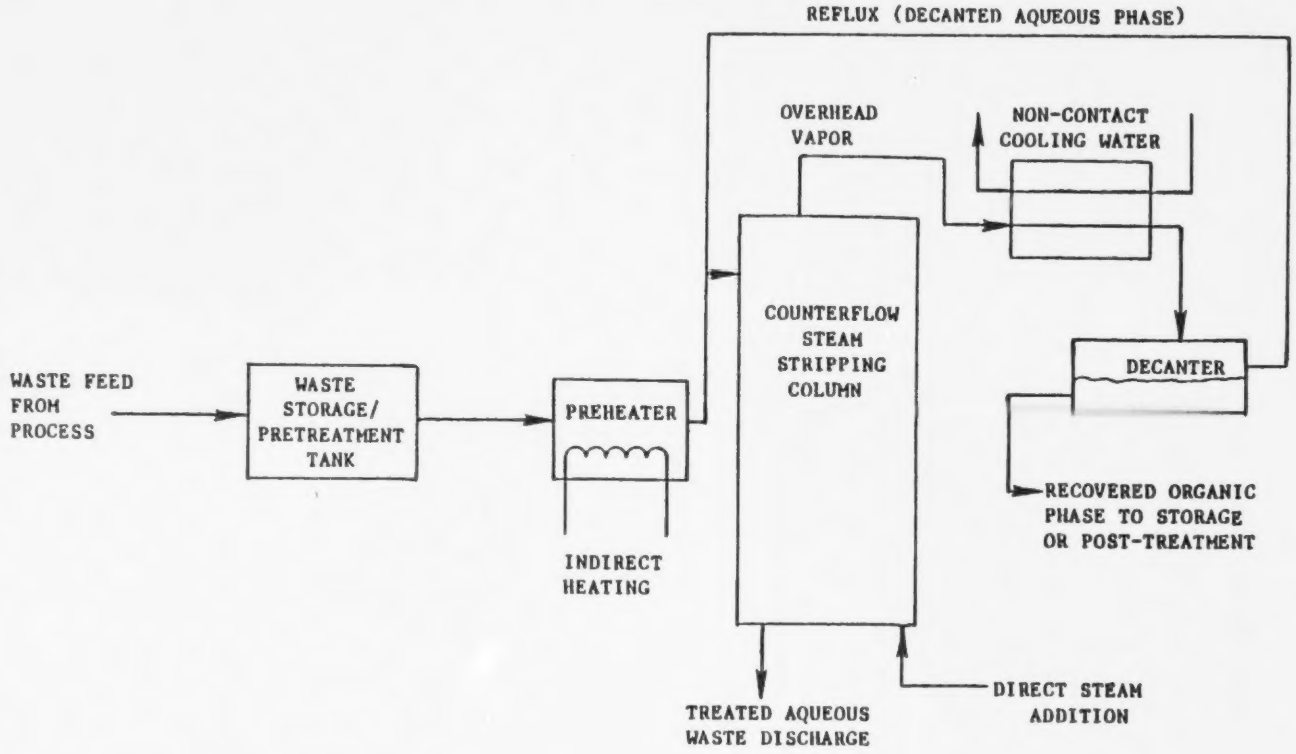
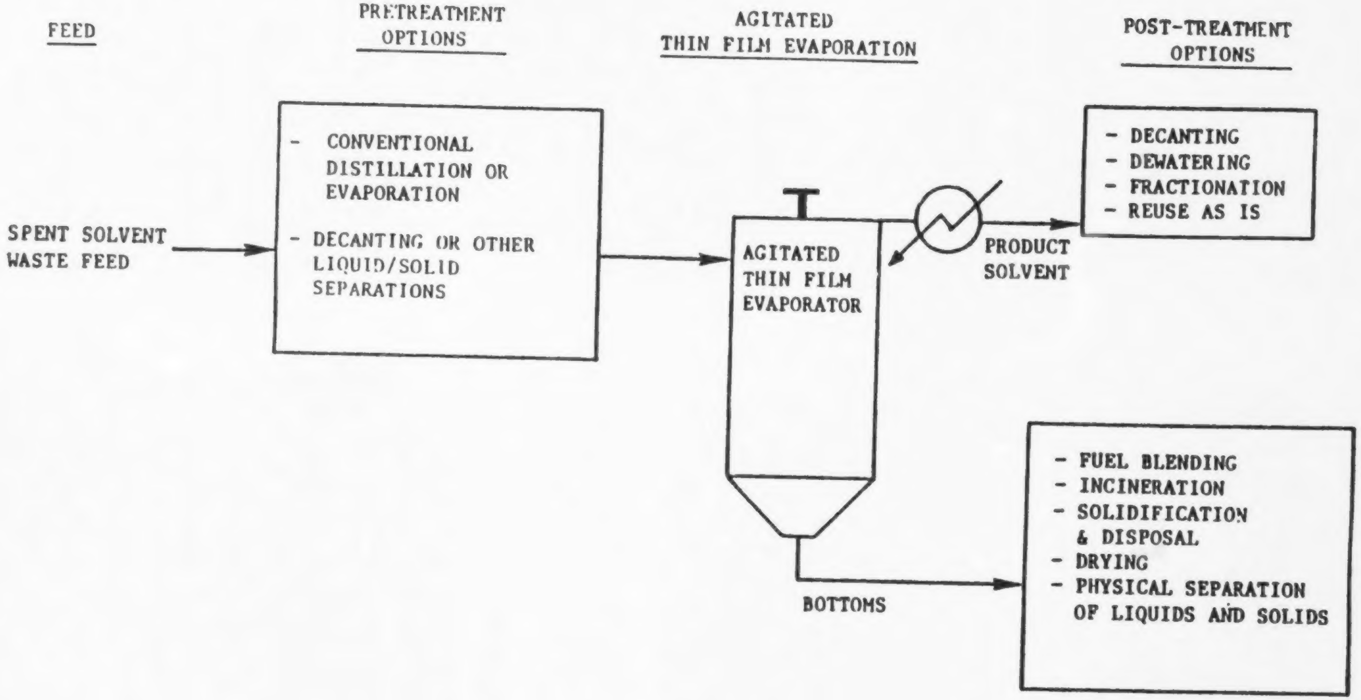

REFLUX (DECANTED AQUEOUS PHASE)
OVERHEAD VAPOR
NON-CONTACT COOLING WATER
WASTE FEED FROM PROCESS
WASTE STORAGE/ PRETREATMENT TANK
PREHEATER
INDIRECT HEATING
COUNTERFLOW STEAM STRIPPING COLUMN
DECANTER
RECOVERED ORGANIC PHASE TO STORAGE OR POST-TREATMENT
TREATED AQUEOUS WASTE DISCHARGE
DIRECT STEAM ADDITION

FIGURE 2. **TREATMENT TRAIN FOR ATFE**


FEED
PRETREATMENT OPTIONS
AGITATED THIN FILM EVAPORATION
POST-TREATMENT OPTIONS
SPENT SOLVENT WASTE FEED
- CONVENTIONAL DISTILLATION OR EVAPORATION
- DECANTING OR OTHER LIQUID/SOLID SEPARATIONS
AGITATED THIN FILM EVAPORATOR
PRODUCT SOLVENT
- DECANTING
- DEWATERING
- FRACTIONATION
- REUSE AS IS
BOTTOMS
- FUEL BLENDING
- INCINERATION
- SOLIDIFICATION & DISPOSAL
- DRYING
- PHYSICAL SEPARATION OF LIQUIDS AND SOLIDS

Post treatment is almost always required. These operations basically include further refinement of the overhead produce through dewatering or fractionation, further solvent recovery, or disposal of bottom products.

The USEPA recently evaluated a thin film evaporator at a recycler which was using the process for the treatment of paint and lacquer thinner. The thinner contains up to 20 percent dissolved paint resins plus suspended pigments and non-halogenated solvents. The overhead product from the ATFE is sold back to the customers without high boiling components, such as xylene. The bottoms product is sold as a waste fuel.

Table 2 displays performance data for the ATFE (6). The unit has 20 square feet of heated surface area with a steam heated jacket. The blades operate at 300 revolutions per minute (rpm) and the unit operates under up to 28 in Hg of vacuum. During the test, the unit processed 1530 gallons of feed material over a 6.75 hour period, generating 830 gallons of distillate product and 688 gallons of still bottoms. Steam pressure was 150 psig and steam temperature was 365°F. Overhead product temperature was 125°F and bottom temperature was 140°F.

Viscosity is the critical waste property that affects thin film evaporator performance. ATFEs can operate in the range of from 1 to 1,000,000 cps.

Fractional Distillation

Distillation is a separation technique that operates on the principle of differential volatility. More volatile constituents can be enriched or separated from less volatile constituents by heating. Distillation can be simple, in which the objective is to concentrate a volatile component, or it can be fractional, in which the goal is to separate two or more volatile components.

Fractionation is a multi-stage process used for separating solvent mixtures when the value of the pure component product justifies the additional processing. As with simple distillation, indirect heat from steam or oil provides the thermal driving force. While simple distillation most often occurs in a pot or kettle, fractionation takes place in a column. Figure 3 is an illustration of a continuous process. In this operation feed is constantly charged to the column at a point which provides the specified top and bottoms product. The section of the tower above the feed point is the rectifying or enriching section and the section below the feed point is the stripping section. A reboiler is connected to the bottom of the fractionation tower to provide the heat needed for additional reflux (condensate recycle) and better fractionation of complex mixture (6).

EPA recently conducted a field test of a full scale batch distillation unit that was used to process a liquid feed containing three major components: methanol, methyl ethyl ketone (MEK), and methylene chloride. The water content of the feed was 3.59 percent. The atmospheric distillation unit was equipped with a 6 foot high, 10 inch diameter packed column and had a batch capacity of 500 gallons.

Table 3 provides data on the performance of the fractionation unit on the three principal constituents. The data in Table 3 shows that the lowest boiling component (methylene chloride) boiled off early, appearing at highest concentrations in the first product cut and decreasing concentrations in subsequent cuts. Methanol concentration in the products was relatively constant. The least volatile of the three major components (MEK) was present in low concentration in the first two cuts and increased in concentration as distillation continued. From Table 3 it can be seen that distillation provides excellent separation for the low boiling point compounds. Further refinement could be achieved through additional product cuts (higher column) or through further distillation of the individual product cuts (7).

Waste Solvent End Use

Waste solvents can be either reused as solvents or burned as fuel. Historically, the extent of solvent recovery has been dictated by equipment processing capability and local marketing situation. However, regulatory constraints imposed on the bottoms product will increasingly become the decisive factor in routing solvents to recovery through treatment.

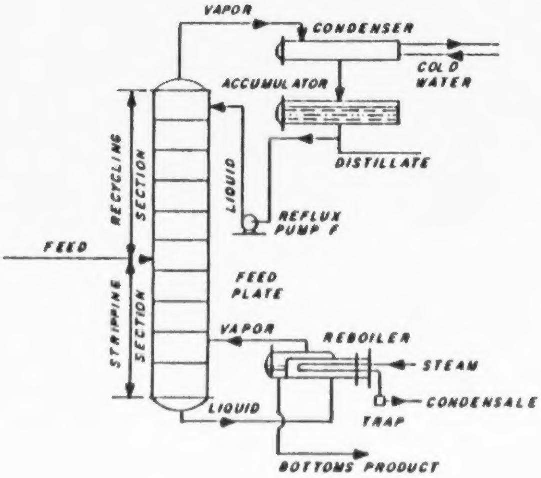

VAPOR
CONDENSER
COLD WATER
ACCUMULATOR
RECYCLING SECTION
LIQUID
DISTILLATE
REFLUX PUMP F
FEED
FEED PLATE
STRIPPING SECTION
VAPOR
REBOILER
STEAM
CONDENSALE
TRAP
LIQUID
BOTTOMS PRODUCT

FIGURE 3. CONTINUOUS FRACTIONATION

TABLE 1. REMOVAL EFFICIENCY DATA FOR STEAM STRIPPER

Compound	Feed Composition (mg/L)	Average Removal Efficiency (Percent)
1,2-Dichloroethylene	1583.3	85.9
Ethylene Dichloride	1593.0	91.3
Dichloromethane	800.9	76.7
1,1,1,2-Tetrachloroethane	572.8	99.9
Chloroform	140.3	89.9

TABLE 2. PERFORMANCE OF THIN FILM EVAPORATION
(All values in mg/kg)

Constituent	Waste Feed	Still Bottoms	Distillate Product
Xylene	66,000	210,000	84,000
Acetone	190,000	5,200	180,000
Ethyl Acetate	11,000	12,000	12,000
Ethyl Benzene	22,000	48,000	28,000
Methyl Isobutyl Ketone	14,000	5,600	16,000
n-Butyl Alcohol	11,000	5,500	13,000
Toluene	220,000	81,000	240,000
Methyl Ethyl Ketone	180,000	57,000	220,000
Isopropanol	76,000	5,500	84,000

TABLE 3. FRACTIONAL DISTILLATION PERFORMANCE

Compound	Boiling Point (°C)	Concentration in g/l					
		Influent	Still Bottoms	Product Cuts			
				1	2	3	4
Methanol	64.5	300	230	160	190	180	190
Methylene Chloride	40.0	460	<0.5	1100	710	590	58
Methyl Ethyl Ketone	79.6	240	370	42	65	280	340

Whether the end use is for solvents or for fuel, the treatment concentration requirements are identical. The decision to further concentrate and/or fractionate will be a function of the relative value of the recovered solvent versus the increased cost of treatment for recovery.

In any case, solvent bottoms will find increasing use as fuels. In 1984, at least 62 percent of solvent bottoms from commercial recovery facilities were used as supplemental fuel.

Commercial Facilities

The commercial solvent recycling industry currently consists of at least 135 firms with 243 facilities in the U.S. Large firms tend to serve regional markets and are capable of producing high-purity solvents through the use of distillation, fractionation, and other specialized recovery techniques. The list below describes solvent recovery technology utilization in the commercial solvent recycling industry (3):

Process	No. of Facilities
Simple distillation	44
Fractionation	22
Thin-film evaporation	43
Steam stripping	18
Drying	17
Solvent extraction	6
Use as fuel	48

Of course, many facilities use combinations of equipment in series to produce a finished product. With the imposition of the land disposal restrictions and the possible constraints to be imposed on deep well injection, both the number of facilities and the adoption of advanced technologies should increase.

Conclusion

Solvent recovery is an important waste management practice today. A greater percentage of solvents are recovered today than any other hazardous waste streams. The degree of purity and selection of end use are not limited by technology but are a function of relative costs of treatment versus product or fuel value. Treatment and disposal costs will rise as land disposal alternatives are eliminated. Therefore, more solvent recovery will be practical in the future.

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EVALUATION OF HAZARDOUS WASTE RECYCLING PROCESSES IN THE PRINTED CIRCUIT BOARD INDUSTRY

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ABSTRACT

In response to the 1984 RCRA Amendments, EPA's Hazardous Waste Engineering Research Laboratory (HWERL) initiated a program to develop case studies demonstrating waste minimization and recycling options for hazardous waste management. The program focused on solvent and metal waste streams from the semiconductor and printed circuit board industries, specifically: 1) waste solvents from resist stripping and developing operations; and 2) metal wastes from plating operations. Two case studies involved the use of solvent distillation units which achieved over 95 percent recovery of spent halogenated solvents. The results suggest that solvent recovery can be widely applied to printed circuit board manufacturing facilities. The other four case studies focused on technologies to reduce metal-plating wastes. Two of these, evaluating the use of sodium borohydride reduction as a substitute for lime/ferrous sulfate precipitation, found that the technology was a viable substitute in one case and was marginally acceptable in another. Another case study, involving carbon adsorption removal of organic contaminants from plating bath wastes, found that this technology significantly reduced both disposal costs and waste volume. A final case study of electrolytic recovery indicated that while acid copper electroplating rinses are amenable to electrolytic recovery, other metal-bearing rinses, such as those from solder (tin/lead) plating or etching are less appropriate.

BACKGROUND

With the enactment of the Hazardous and Solid Waste Amendments (HSWA) in November 1984, Congress set forth a schedule for evaluating the land disposal restriction of various classes of hazardous wastes including: (1) solvents; (2) metals and cyanides; (3) halogenated organics; (4) corrosives; and (5) dioxin wastes. A key issue identified in the evaluation of the waste bans is the availability of commercial treatment capacity to handle the wastes proposed for banning. Therefore,Congress also asked EPA to evaluate the potential for onsite waste minimization to reduce the quantity or toxicity of wastes being considered under the ban.

In an effort to identify successful waste minimization technologies, EPA's Office of Solid Waste (OSW) and Office of Research and Development (ORD) Hazardous Waste Engineering Research Laboratory (HWERL) set forth on research efforts aimed at assessing the viability of waste minimization as a means of reducing the quantities of land disposed hazardous waste. OSW's research focused on an exhaustive literature review identifying a broad spectrum of waste minimization technologies and their various applications. The primary emphasis of HWERL's work was on demonstrating the effectiveness of specific minimization technologies through case studies and process sampling.

INTRODUCTION

The purpose of this project was to evaluate the effectiveness of various waste minimization practices or technologies in the printed circuit board and semiconductor manufacturing industries. The most significant waste streams in these industries are waste halogenated solvents from photoresist stripping and developing operations (RCRA Waste Code F001-F003), and metal-bearing sludges (RCRA Waste Code F006) from the treatment of metal plating and etching rinsewaters. This paper presents the findings of case studies conducted at five printed circuit board manufacturing facilities and one commercial treatment/recovery facility. Each facility investigated employs some practice that requires offsite disposal. Two of the case studies focus on the recovery of spent halogenated solvents, and the remaining four discuss the recovery or reduction of metal plating and etching process wastes. Table 1 summarizes characteristics of facilities investigated which range from small job shops to large integrated facilities.

The common objectives of each of the technologies evaluated are:
(1) minimization of metals sludges generated; (2) compliance with effluent guidelines or local discharge limitations; and (3) reduction in operating costs over other conventional alternatives. The following discussion briefly summarizes each case study, the nature of the minimization technology, the measurements data collected and the results obtained.

METAL PLATING BATH WASTE MINIMIZATION CASE STUDY RESULTS

Metal plating wastes generated from plating bath dumps, rinses, etching machines and scrubbing operations generate copper-, nickel-, tin-, and lead-contaminated wastes. Four of the six case studies investigated under this research project focus on the minimization of sludges generated primarily by copper plating and etchant baths and copper and tin/lead rinsewaters.

Facility A Case Study

Description--

Facility A is an offsite Treatment, Storage, and Disposal (TSDF) facility which processes concentrated dumps from the metal plating and printed circuit board industries, including alkaline etchants, acid plating baths, nitric acid rack strip baths, and electroless plating cyanide baths. The average total metals concentration in the incoming waste was reportedly 12 g/L (12,000 ppm). Initially, the facility was designed to operate using lime and ferrous sulfate precipitation of

TABLE 1. SUMMARY OF FACILITIES TESTED UNDER WASTE MINIMIZATION CASE STUDY PROGRAM

Facility name	Description	Wastes treated/reduced	Technology	Residuals
Facility A	Treatment storage disposal facility handling electroplating baths, waste etchants, spills, etc. Capacity: 1,000 gph (24,000 gpd).	- Nickel plating baths - Copper plating baths - Cyanide	- Sodium hydroxide precipitation - Sodium borohydride reduction - Alkaline chlorination	Sludge product
Facility B	Contract PC board manufacturing shop Employees: 77 Production: 500,000 ft^2/yr Sales: $7 Million/yr	- Cupric chloride etchant - Electroless plating rinses - Electroplating rinses	- Sodium borohydride reduction - Memtek ultrafiltration system	Sludge product
Facility C	Computer manufacturer. Employees: 10,000	- Methyl chloroform resist developer - Freon resist developer	- Solvent distillation/fractionation recovery of resist developers.	Still bottoms
Facility D	Electronic equipment mfgr. PC board manufacturing using the subtractive technique in the MacDermid process. Employees: 260	- 1,1,1-trichloroethane resist developer - 1,1,1-trichloroethane still bottoms	- 2-stage solvent distillation - (1) DuPont RISTON SRS-120 solvent recovery still - (2) Recyclene Products, Inc. RX-35 still	Still bottoms
Facility E	Computer manufacturer. PC board manufacturing using additive techniques. Employees: 600 Production: 600,000 ft^2/yr	- Acid copper plating bath	- Activated carbon regeneration of spent plating baths.	Spent activated carbon
Facility F	PC Board manufacturer. 2-sided single layer circuit boards. Production: 480,000 ft^2/yr	- Acid copper plating rinsewaters - Tin/lead plating rinsewaters	- Agmet Equipment Corp. - electrolytic recovery units.	Metal foil

metals as the primary means of waste treatment. When the high cost of land disposal of the lime sludges was considered, alternate means of treating and disposing of the waste were evaluated.

The unit processes selected to detoxify the wastes and recover metals at Plant A currently include sodium hypochlorite oxidation of cyanides (alkaline chlorination), sodium hydroxide precipitation, pH adjustment, sodium borohydride reduction (with sodium metabisulfite stabilization), sedimentation, plate and frame filter press (for sludge dewatering), rapid sand filtration, and ion exchange columns for effluent polishing.

Results--

The primary purpose of the Facility A case study was to evaluate sodium borohydride as a viable waste treatment alternative for reducing RCRA Hazardous Waste Code F006 spent electroplating baths. The evaluation criteria were the ability of sodium borohydride (SBH) to effectively meet local compliance standards and produce a high density, low-volume sludge. The test program evaluation relies mainly on the trace metals results to evaluate system performance.

The SBH reactor was sampled for eight selected metals on the influent, effluent, and sludge streams. Analytical results demonstrated individual metal reduction efficiencies which ranged from 16.1 to 99.8 percent. The observed range in efficiency data was attributed to variations in concentration and chemical potential (quantity of free energy required for an ionic species to obtain equilibrium) of each of the metallic ions contained in the solution. Overall, SBH was able to reduce 6.91 kg of the initial influent metals loading of 7.25 kg. These results represent a greater than 95 percent reduction in total metals for a complex waste stream. The remainder of the metals influent loading (0.337 kg) consisted of over 70 percent calcium.

An additional objective of this program was to evaluate the ability of Facility A to consistently meet local pretreatment requirements. The resultant data for two separate batch runs showed discharges in excess of effluent limits, apparently due to incomplete polishing caused by cation exchange column breakthrough. Since the test program was completed, Facility A has instituted the use of a quality control holding tank and further waste processing optimization to remedy these problems. Follow-up discussions with the local sewer authority revealed that Facility A's effluent quality has improved considerably and is now consistently meeting compliance guidelines.

In addition to assessing wastewater effluent characteristics, the testing program was designed to evaluate uncontrolled process air emissions. The results were obtained by Draeger tube analysis of grab and integrated samples of exhaust gases taken from the process reactor exhaust ducts. The emission results showed a frequent presence of hydrochloric acid and hydrogen gas accompanied by occasional presence of ammonia and sulfur dioxide. One of the hydrogen emissions grab sample results (6.0 percent) is significant since this value is greater than the lower flammable limit for hydrogen (4.0 percent). Grab sample concentrations for ammonia and sulfur dioxide also exceeded adopted short-term exposure limits (STEL) for these substances.

Due to SBH sludge filter press operational difficulties, realistic data as to SBH's ability to produce a high density, low volume sludge was unobtainable. However, EP toxicity analyses of the sludge produced indicated that for Facility A influent metals concentrations, the SBH sludge produced is fairly stable in that its leachate characteristics are below EP Toxicity limits for all metals. However, note that the waste is still classified as F006 hazardous waste.

An additional objective of the Facility A case study was to evaluate the ability of sodium borohydride to economically reduce F006 waste streams. At the time of testing, Facility A reduction chemistry was very inefficient at $19.8/lb of copper reduced. However, through process optimization, chemical costs have reportedly decreased over 63 percent,[1] bringing process economics within acceptable limits. The case study follow-up for Facility A has indicated that the cost of copper reduction has been lowered to $7.27/lb of copper.

Facility B Case Study

Description--

Facility B is a captive printed circuit board manufacturing facility. Production at Facility B uses a special hybrid process, employing elements of both additive and semi-additive printed circuit production techniques. Facility B uses a slow acting etchant (sodium chloride, sodium chlorate, and muriatic acid) which etches copper from the board, and yields cupric chloride in the waste stream.

Facility B uses a unique end-of-pipe treatment system employing sodium borohydride treatment and ultrafiltration (Memtek) technology for solids separation. In this process, incoming plating and etching wastes are adjusted to pH 7-11 by addition of sodium hydroxide or sulfuric acid. Sodium borohydride is added to obtain an oxidation reduction potential (ORP) of approximately -250 mv or less. The reacted waste then feeds from the concentration tank to a Memtek ultrafiltration unit from which the permeate is discharged to municipal treatment, and the concentrate is returned to the concentration tank. A small plate and frame sludge filter press dewaters the sludge which is drawn from the bottom of the concentration tank.

Points of interest in evaluating the Facility B waste treatment system for this case study were: (1) compliance of the ultrafiltration permeate (wastewater discharge) with local and Federal discharge standards; (2) the volume and EP toxicity of the sludge filter cake; and (3) economic evaluation against comparable technology (lime and ferrous sulfate treatment).

Results--

Analysis of the influent and effluent streams metals characteristics, showed that copper was reduced most efficiently (99.82 percent), while nickel reduction was the least efficient at (45.5 percent). Differences in removal efficiencies were attributed to variations in concentration (higher removals for higher concentrations), but the chemical potential may also have been a factor. Approximately 144.7 lbs of combined metals were reduced to elemental form by the SBH reaction system, representing a combined reaction efficiency of 99.8 percent. Despite deviations from design operating conditions, the SBH/ultrafiltration system performed very well. EP Toxicity leachate test results for Facility B filter press sludge clearly show that the sodium borohydride sludge produced is fairly stable with leachate characteristics below EP Toxicity limits for all metals.

An economic comparison of the use of sodium borohydride versus lime-ferrous sulfate chemistries was conducted. The results demonstrate that in this application, sodium borohydride would be superior to lime-ferrous sulfate for the following reasons: (1) sludge disposal costs and volumes would be reduced by 93.5 percent; (2) overall operating expenses would be 48 percent lower; and (3) sludge generated by the SBH reduction process was 78 percent copper and suitable for reclamation (due to the high copper content). Note that the use of the sodium borohydride and ultrafiltration treatment at Facility B is favored by the use of the sodium chloride etch process in lieu of the more commonly preferred ammonium chloride etch process. The ammonium-based etchants create borohydride sludge reduction problems which require tighter treatment process control and the use of primary reductants such as sodium metabisulfite. Additional factors which favor the economics of sodium borohydride treatment at Facility B include: 1) high copper concentrations and low organic loadings; and 2) low effluent limitations required by the sanitation district.

Facility E Case Study

Description--

In Facility E plating operations, addition agent and photoresist breakdown products incrementally accumulate and contaminate electrolytic (charge carrying) plating baths. In the absence of a bath regeneration system, Facility E would typically be forced to either discharge the spent plating bath to the wastewater treatment plant or send it offsite for disposal. In either case, large quantities of metals containing sludge (RCRA Waste Code F006) would be generated and subsequently land disposed. Instead, Facility E regenerates the spent plating baths through activated carbon filtration (used to remove built-up organic bath contaminants) and then returns them to the process. The frequency of cleaning is determined by organic contaminant build-up. Electroplating baths never have to be dumped with this arrangement under normal processing conditions.

Activated carbon treatment is performed in a batch mode for acid copper, solder and nickel microplating baths in three separate systems. The bath reclamation system consists of a holding tank, mixing tank, and MEFIAG paper-assisted filter. For acid copper treatment, 2,400 gallons of contaminated solution is pumped into a 3,000 gallon mixing tank. Hydrogen peroxide is added and the temperature of the bath is maintained at 120 to 130°F for 1 hour. Powdered activated carbon (80 lbs) is added and the contents are mixed for 3 to 4 hours to oxidize volatile organic species. The solution is recirculated through a paper-lined MEFIAG filter several times to remove the activated carbon. The filter solids and paper are removed as needed when a predetermined pressure drop across the filter is reached. When the bulk of the activated carbon has been removed (generally after three passes of the solution through the filter), the filter is precoated with 5 gallons of diatomaceous earth. The solution is again recirculated through the filter until a particulate test indicates sufficient solids removal (no residue detected on visual examination of laboratory filter paper). Total spent solids from plating bath purification is 1-1/2 drums every 3 months which is landfilled.

Results--

The purpose of this case study was to evaluate the extension of electroplating bath lifetimes (and subsequent waste reduction) by activated carbon removal of organic brightener breakdown products. The acid copper baths were selected for study since recovery of this solution results in the most significant amount of waste minimization.

Sampling and analysis was conducted on three process streams associated with activated carbon bath reclamation. Based on resultant analytical data the following conclusions were drawn: 1) forty-seven percent of the organic by-products and brighteners were removed from the contaminated solution; 2) low molecular weight organics such as carboxylic acid derivatives are not preferentially adsorbed; 3) reduced sulfur (a brightening and leveling agent) is oxidized and volatilized during treatment; and 4) inorganic contaminants such as tin and lead are also removed (37.5 percent and 24.5 percent, respectively) as a beneficial by-product of the treatment process.

In recovering spent electrolytic plating baths, Facility E was able to save over $50,000 in hazardous waste disposal and raw material purchase costs. These savings represent a payback period of only 3 months for purchasing the activated carbon recovery system.

Facility F Case Study

Description--

Prior to implementation of the electrolytic recovery technology at Facility F, plating and etching rinsewaters contained copper and lead at concentrations of up to 3,000 mg/L. The facility converted several rinse tanks into static dragout tanks and installed these at the copper and tin/lead rinse baths where there was the most potential for metal recovery.

The electrolytic reactors used at this facility were Agmet Equipment Corp., Model 5200 reactors. They consist of a wastewater sump, a pump, and a rectangular reactor with dimensions of approximately 22 in. x 10 in. x 22 in. The reactor consists of a cylindrical anode encircled by a stainless steel cathode with a diameter of 8 in. and a height of 6 in. The anode material used for copper plating solutions was titanium, while a columbium anode was required for tin/lead plating solutions because the fluoroboric acid in the tin/lead plating solution was extremely corrosive to titanium. The columbium anode increases the cost of these electrolytic units to $4,500, as opposed to $3,500 for the titanium anode units.

Results--

At the time of testing, four electrolytic reactors were being used for recovery of copper, and three were being used for recovery of tin/lead. To evaluate the performance of these units, samples of the plating bath, dragout, and rinse bath were analyzed.

The following conclusions were drawn based on the resultant data. Recovery rate of copper from the acid copper solution was approximately 4 to 5 grams/hour/unit, representing an efficiency of nearly 90 percent. The investigators also noted that concentrations of tin and lead in the dragout were not significantly less than those in the plating bath indicating a poor level of recovery. Thus, use of in-line electrolytic recovery was not able to reduce metal concentrations sufficiently to enable this facility to meet pretreatment standards.

Electrolytic recovery would significantly reduce the amount of sludge generated if a lime precipitation system were utilized to remove metals from the final plant effluent. For this facility, a reduction and subsequent waste minimization of 32 tons/year would be realized. At a sludge disposal cost of $200/ton, the annual cost of electrolytic recovery would exceed the savings. However, if sludge disposal costs increased to $300/ton, the savings (at least for copper recovery) would exceed the processing costs.

RESIST DEVELOPING SOLVENT RECOVERY CASE STUDIES

Two case studies evaluated under this program focused upon the minimization of developer solvent wastes and sludges which might require either land disposal or incineration. In the case of Facility C, the technology involves the separation of a two-solvent system with subsequent recovery and reuse of each solvent. In the case of Facility D, the technology evaluated further recovers the solvent bottoms product of the initial recovery unit.

Facility C Case Study

Description--

The spent solvents from photoresist stripping and developing are contaminated with photoresist solids at up to 1 percent, and the solvents used for surface cleaning are contaminated by dust, dirt or grease. Waste solvents are recovered at Plant C by distillation or evaporation and returned to the process in which they were used. Several types of equipment are used including flash evaporators to recover methyl chloroform, and a distillation column to recover Freon.

There are two identical flash evaporators at the facility, each with a capacity to recover 600 gallons of methyl chloroform (MCF) per hour. The flash chamber operates at a vacuum of 20 in. Hg, allowing the MCF to vaporize at 100 to 110°F. The units are operated one to two shifts/day depending on the quantity of waste solvent being generated.

A packed distillation column is used to recover pure Freon from a waste solvent stream containing approximately 90 percent freon and 10 percent methyl chloroform. Waste is continuously fed to a reboiler where it is vaporized and rises up the packed column. Vaporized freon passes through the column, is condensed and recovered at a rate of 33 gal/hour. MCF condenses on the packing and falls back into the reboiler. The distillation bottoms are removed when the concentration of methyl chloroform reaches 80 percent (approximately 1 to 2 weeks).

Results--

Sampling and analysis was conducted on process streams associated with the solvent recovery processes. One of these processes was the flash evaporator used for recovery of methyl chloroform (1,1,1-trichloroethane), and the other was the distillation column used to recover Freon from a Freon/methyl chloroform mixture. The conclusions drawn from the sampling and testing program were: 1) at least 95 percent of the solids are removed from the solvent waste influent; 2) the recovered product is at least as clean as the virgin material; and 3) the still bottoms from recovery of contaminated solvent still contain a high fraction (90 percent) of solvent.

In recovering spent solvent, the company saves over $10 million annually, compared to offsite recovery. The savings per pound of methyl chloroform, methylene chloride, and Freon recovered is $0.18, $0.18, and $0.61, respectively. The high cost savings are primarily due to the fact that the solvents recovered are reused onsite, thus reducing the quantity (by greater than 95 percent) of new or virgin solvent that must be purchased. Because the rate of generation of spent solvent is so high, the initial expense of purchasing recovery equipment is quickly returned.

Incentives other than economic reasons for onsite recovery include: 1) reduction in the risk of a spill of solvent in transporting the waste to a TSDF; and 2) reduced liability related to an accident at the TSDF resulting in the release of spent solvent.

Facility D Case Study

Description--

Printed circuit boards are produced at Facility D using the subtractive technique and solvent-based photoresists. Methylene chloride resist stripper and 1,1,1-trichloroethane (TCE) developer are continuously recycled in closed-loop stills. The TCE developer wastes (Waste Code F002) are recovered in a DuPont Riston SRS-120 solvent recovery still (referred to as the primary still) and returned to the developer line. Until recently, all still bottoms from the primary still were drummed and shipped offsite for reclamation at a solvent recycling facility. Facility D purchased a Recyclene Industries RX-35 solvent recovery system (referred to as the secondary still) in October 1985, to recover additional TCE from the SRS-120 still bottoms.

The Recyclene Industries RX-35 solvent recovery system is a batch distillation system with a 30 gallon capacity, silicone oil immersion heated stainless steel boiler, a noncontact, water-cooled condenser, and a 10 gallon temporary storage tank. The boiler is equipped with a vinyl liner inside a Teflon bag. The Teflon bag provides temperature resistance and the vinyl bag collects solid residue, eliminating boiler clean-out and minimizing sludge generation after distillation. Two thermostats control the temperature of the boiler and the vapor, automatically shutting down the boiler when all the solvent has evaporated. The maximum operating temperature of the still is 370°F, so recovery of solvents with higher boiling points would not be practical. Recovery of a 20 to 25 gallon batch of still bottoms requires approximately 90 minutes at Facility D, and four to six batches are completed each day.

Results--

Evaluation of the system consisted of the analysis of the contaminated feed, overhead product, and distillation bottoms. Based on a mass balance and analytical data, the following conclusions were made: 1) purity of recovered solvent was 99.99 percent; 2) total solvent recovery was 99.78 percent; 3) Still bottoms contained 7.5 weight percent 1,1,1-trichloroethane; and 4) reduction in waste generation was 97.5 percent..

Annual cost savings ($43,000) and waste reduction (10,602 gal) were calculated for Plant D, based on the first year of RX-35 operation. In addition, the investment payback period for the RX-35 was calculated considering credit for reclaimed solvent and reductions in waste transportation and disposal costs. The estimated payback period was 7.3 months, given the current level of solvent reclamation. Thus, the low capital cost of the unit and the relatively high costs of virgin solvent ($4.50/gal) favor the second-stage recovery of TCE developer still bottoms.

Potential drawbacks to the implementation for a RX-35 back still include 1) while this technology significantly reduces the volume and toxicity of the solvent still bottoms, it continues to generate a hazardous waste product, 2) there is a large potential for the accumulation of contaminants and/or breakdown products.

SUMMARY OF FINDINGS

The findings of the waste minimization case studies evaluated under this program are presented in Table 2, which includes data collected by the facilities and verified by sampling and laboratory results. These results indicate that a good variety of technologies exist to minimize metals-containing and solvent wastes produced by the printed circuit board and semiconductor industries. The technologies discussed range from simple changes in treatment system reagents with nominal capital costs to large onsite solvent reclamation facilities with significantly higher capital costs.

TABLE 2. SUMMARY OF FINDINGS OF WASTE REDUCTION/RECYCLING CASE STUDIES

Facility name	Technology	Waste reduction	Annual waste reduction achieved	Capital costs ($)	Projected annual cost savings ($)
Facility A	Sodium borohydride reduction	Metals sludge	--[a]	Nominal	--[b]
Facility B	Sodium borohydride reduction	Metals sludge	962 tons	Nominal	115,870
Facility C	Solvent batch distillation	Methylene chloride Methyl chloroform Freon	6,152,000 gal	709,400	16,000,000
Facility D	2-Stage solvent distillation	1,1,1-Trichloroethane Resist developer still bottoms	10,625 gal	26,150	43,105
Facility E	Carbon adsorption plating bath reclamation	Plating bath wastes (metals sludge)	10,600 gal	9,200	57,267
Facility F	Agmet electrolytic recovery unit	Metals sludge	32 tons	30,350	(10,685)[c]

[a] Not quantifiable, but a significant waste reduction was realized.

[b] Not demonstrated during testing.

[c] ( ) indicates negative value.

Four of the case studies investigated under this program focused on technologies to reduce metal-plating rinsewater sludges. The use of sodium borohydride as a substitute for lime/ferrous sulfate was found to be viable in one case and appeared to be marginally acceptable in another. The case study on carbon adsorption recovery of plating bath wastes found that this technology significantly reduced both disposal costs and waste volume. The case study of electrolytic recovery indicated that this technology is highly waste stream specific. An acid copper electroplating rinse is an ideal waste stream for electrolytic recovery. However, other metal-bearing rinses, such as those from solder (tin/lead) plating or etching, are not appropriate for use of electrolytic recovery. Electrolytic recovery units are, however, generally inexpensive to purchase and can be used in many cases to supplement an end-of-pipe treatment process.

Two of the case studies presented in this paper involve the recovery of spent halogenated solvents using solvent distillation units. Both of these case studies indicate that onsite solvent recovery is successful from a technical and an economic standpoint. In both cases, over 95 percent of the waste solvent was recovered and reused onsite. Solvent recovery appears to be a technology that could be applied to a number of printed circuit board manufacturing facilities.

The results of this project indicate that waste reduction can be achieved through the use of appropriate technology, and it can be achieved with significant reductions in cost. The case studies also indicate that the success of waste reduction is in many cases waste stream specific. The technologies will not necessarily be successful in all cases. A slight variation between one waste stream and another may make waste reduction either technically or economically impractical. Therefore, successful waste reduction is dependent on a thorough knowledge of waste quantities and characteristics.

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THE CALIFORNIA INNOVATIVE ALTERNATIVE TREATMENT AND RECYCLING DEMONSTRATION PROJECTS PROGRAM

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ABSTRACT

The California Department of Health Services in cooperation with the U.S. Environmental Protection Agency is conducting, as part of its broad waste reduction program, demonstrations of alternative technologies and studies on hazardous waste management. The overall objective of the California Waste Reduction Program is to reduce the amount and eventually eliminate land disposal of untreated hazardous wastes. Alternative waste management strategies being studied include, in order of preference, (1) source reduction, (2) recycling, and (3) treatment.

This paper discusses state and federal statutory requirements and problems encountered in the process of implementation of the elements of California's Waste Reduction Program. Specific studies described include (1) waste stream information collection, (2) assessment of extent of use of waste treatment in California, (3) waste audit programs, (4) waste management information transfer, and (5) discussion of preliminary results from demonstration projects.

INTRODUCTION

The California Department of Health Services' Waste Reduction Program was initiated in July, 1984. The program has been developed with input from environmental groups and industry. In addition, the Department has reviewed the efforts of waste reduction programs from six states and incorporated their regulations which were applicable to California. The various program elements are designed to overcome different technical and financial barriers, to help facilitate permitting, and to meet regulatory requirements. These key elements include (1) technical assistance, (2) information and technology transfer, (3) economic incentives, and (4) regulatory incentives.

The major waste reduction strategies of the California Waste Reduction Program that industry can apply to reduce the volume of untreated hazardous wastes going to land disposal in order of preference are: (1) Source reduction--the elimination or reduction of the generation of hazardous wastes; (2) Recycling and reuse--reprocessing of a waste material to a point that it can be used again for the original or different purposes; (3) Treatment--including incineration to eliminate or reduce the hazardous characteristics of wastes; and (4) Limit land disposal to treated wastes residues only.

Source reduction is the best solution as it eliminates the problems associated with hazardous waste generation, storage, transportation, treatment, and residual disposal. This strategy reduces significantly the volume of hazardous wastes and can usually be accomplished by improvements in the manufacturing process, waste stream segregation, and handling. Its implementation beyond a certain point may require major technological changes and may become too costly to implement. Also, treatment and disposal of the reduced volume of the waste will still be required.

Recycling feasibility for different wastes is affected by costs of raw materials, cost of disposal alternatives, and specific process demands. The availability of low-cost raw materials in comparison with the cost of recycled wastes may limit this option.

Treatment has the potential to detoxify most wastes although it may shift the public health and environmental risks from land to air, ground and surface waters. Treatment usually results in a residue less toxic than the original wastes which can then be disposed in a non-hazardous waste landfill. However, there are some instances where a smaller volume of highly concentrated waste is produced which will require disposal in a hazardous waste landfill.

A major part of the waste reduction program has involved the EPA in a Cooperative Agreement with the Department of Health Services (DHS). This three year multi-task project, started in 1985, and under the supervision of Mr. Harry Freeman of EPA's Hazardous Waste Engineering Research Laboratory, has provided the Department with staff and contractual support. Projects related to the program include: (1) Waste Reduction (Minimization), (2) Technical Information Dissemination, (3) Evaluation of Potential Economic Incentives, (4) Land Restrictions Impact on Management of Restricted Wastes, and (5) On-site Small Treatment Demonstration Program.

This paper will discuss the specific studies made possible by the EPA Cooperative Agreement as well as state and federal statutory requirements and problems encountered in the process of implementing the elements of California's Waste Management Program.

REGULATORY INCENTIVES AND STATUTORY MANDATES

Regulatory Incentives

The regulatory element of the Waste Reduction Program provides a major driving force for moving industry towards alternatives to land disposal. In addition, it provides some of the necessary tools for the Department to effectively implement the technical assistance and information transfer components of the program. Given this, the Department has set the following objectives: (1) to provide a clear message that hazardous waste management in California must move towards waste reduction and away from land disposal; (2) to ensure utilization of available technology for hazardous waste treatment; (3) to require that industry be aware of and consider waste reduction whenever possible, and (4) to expand the California land disposal restriction program to coincide with the federal land disposal restrictions program.

California Land Disposal Restrictions Program

California's Land Disposal Restriction Program was initiated in December 1982, when the Department implemented a regulatory program to phase out land disposal of certain hazardous wastes. This program provided a schedule of land disposal restrictions for specific hazardous wastes, the California List, to be implemented, contingent upon the availability of alternative treatment and/or recycling capacity in the State. The restricted liquid wastes and implementation schedule dates include: (1) free cyanides greater than 1000 mg/L (6-1-83); (2) dissolved metals, compounds, elements containing arsenic, cadmium, chromium, lead, mercury, nickel, selenium, or thallium (1-1-84); (3) acid wastes with a pH less than 2.0 (1-1-84); (4) PCB's greater than 50 mg/L (1-1-84); and (5) wastes containing halogenated organic compounds greater than 1,000 mg/L (1-8-85).

An additional land disposal restriction for solid hazardous wastes containing halogenated compounds in total concentration greater than 1,000 mg/L is scheduled to go into effect 7-8-87. Another requirement of Senate Bill 509 (Carpenter, 1985), restricts hazardous wastes having a heating value of 3,000 BTU's per pound, to incineration or treatment as the only means of disposal, will go into effect on 1-1-88. Other regulations restricting land disposal of hazardous waste containing volatile organics above a range of one to eight percent (to be specified) are to be developed by the Department on or before 1-1-90.

Federal Land Disposal Restrictions

Section 3004 of the Resource Conservation & Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA), prohibits the continued placement of RCRA-regulated hazardous wastes in or on the land, including placement in landfills, land treatment areas, waste piles, and surface impoundments (with certain exceptions used for the treatment of hazardous wastes). The amendments specify dates by which these prohibitions are to take effect for specific hazardous wastes with May 8, 1990, being the deadline for the last third of all RCRA listed wastes. The wastes restricted and schedule dates are as follows: (1) bulk liquids: 5-8-85; (2) solvent waste: 11-8-86; (3) California List: 7-8-87; (4) first third of all RCRA listed wastes, decision on underground injection, clean up wastes subject to retrictions: 8-8-87; (5) dioxin containing wastes (catagories F020 to F028): 11-8-88; (6) second third of all RCRA listed wastes: 6-8-89; and (7) last third of all RCRA listed wastes: 1-1-90.

Implementation of these state and federal mandates has been impeded by a number of problems. The first problem area is inadequate waste composition and volume information. Without this information it is extremely difficult for the state and industry to assess the potential for waste reduction, facility needs, and compliance with land disposal restrictions. The second problem area is the lack of performance data from different demonstration treatment technology projects. Industries, regulatory agencies, and the public are seeking information related to the evaluation of technologies before extensive funds and time are invested and before the technology becomes a permanent fixture in an area.

The third area of concern limiting the implementation of waste reduction programs is the limited number of off-site treatment facilities in the state. The siting and regulatory requirements and the difficulty in obtaining environmental and liability insurance have severely limited the number of on-line treatment facilities in California. Today there is a lack of incineration treatment capacity and only one off-site operating hazardous waste treatment facility in the state, General Portland.

The Waste Reduction Program is addressing these implementation problems with the following projects: (1) Waste stream information accumulation and analysis; (2) Determination of extent and use of on-site treatment; (3) Waste audit program; (4) Waste management information transfer; and (5) Demonstration studies. These are presented below.

Waste Stream Information Accumulation and Analysis

Hazardous waste generators and operators of treatment, storage, and disposal facilities in California must now submit reports to the Department that identify the type and quantity of hazardous wastes shipped off-site or wastes they have handled. In addition, the Department has also requested more specific information pertaining to the constituents and concentrations of materials in their waste streams. These reporting requirements should improve the Department's and industry's ability to assess the potential for waste reduction, facility needs, and compliance with the land disposal restrictions.

As part of this program, the Department of Chemical Engineering at the University of California, Davis, is assisting the Department to characterize California's waste streams in terms of their suitability to various treatment, recycling, and reduction processes. Over 11,000 individual waste stream description reports, containing information on constituents and concentrations of different wastes, will be analyzed. The principal tasks are to: (1) prepare protocol for analyzing the data according to specific criteria for a particular treatment, recycling, or reduction process; (2) develop an easy access data base format; (3) prepare an analyses of this year's data, and (4) prepare recommendations for future waste stream description forms. A final report will be available in Fall, 1987.

Determination Of On-site Treatment Use

The Department has reviewed the 1985 Biennial Facility Reports submitted on EPA's forms. Although useful, some of the major problems with the EPA biennial facility reports were identified as follows: (1) no correlation existed between the amount of hazardous wastes received and the ultimate disposal; (2) discrepancies in report form's disposal codes and disposal codes in 40 CFR; (3) no code for recycling of wastes with subsequent reporting recycling as storage; (4) misunderstanding in reporting due to similarities in appearance of facility reporting forms and generator's report forms; and (5) double counting of hazardous wastes created by generators reporting on-site storage as disposal and then having TSD facilities claiming these wastes as well. Staff has redesigned the form and the Department will be using this in 1986 data gathering via the Annual Facility Report due March 1, 1987.

After review and discussion of the EPA reports, California reporting requirements have been modified to be consistent with federal law and also improved to obtain more complete and accurate information. Hazardous waste generators must now submit a biennial report to the Department that covers the type and quantity of hazardous waste shipped off site. Operators of treatment, storage, and disposal facilities must submit similar reports on the wastes they have handled. The Department has, in the forms provided to the generators and operators, requested additional information on the constituents and concentrations of materials in their waste streams. These reporting requirements will improve the Department's ability to assess potential for waste reduction, facility needs, and compliance with the land disposal restrictions.

Another reporting provision which came into effect with the passage of Assembly Bill 685 (Farr, 1985) requires that generators describe, in their biennial reports, waste reduction efforts and changes in waste generation from the previous year. These reports will assist the Department in developing information on effective waste reduction projects and an assessment of waste reduction potential for specific industries.

New reporting requirements for generators concern changes to the Uniform Hazardous Waste Manifest. Generators shipping waste off site must now sign a certification form which states that a program to reduce the volume and toxicity of waste generated to the degree determined to be economically feasible is in place and the method of treatment, storage, or disposal currently available which minimizes the present and future threat to humans and the environment has been selected.

After the above information is collected and analyzed, the Department will be able to predict how much hazardous waste is produced in California, how much is being disposed on land, and what remaining disposal capacity exists in the state. Projections can then be made as to the types and volumes of wastes which will be impacted and what types and scale of storage, recycling, and treatment facilities will be needed.

WASTE AUDIT PROGRAM

The Department has been administering a program to provide technical assistance for California industries as part of its coordination, research, and development efforts to promote reduction or recycling of hazardous wastes. This program includes the Waste Audit Studies for hazardous waste generators targeting various industries. Each waste audit study will focus on a specific industry and include an on-site evaluation of three to six firms within that industry. For each firm, the manufacturing process and/or operating systems will be audited, and the current waste management practices will be appraised to identify options that could be utilized to recycle, treat, or reduce the generation of hazardous wastes.

The first set of waste audit study contracts for approximately $25,000 each were awarded in March, 1986, for the following: (1) pesticide formulators, (2) paint industry, (3) circuit board manufacturers, (4) automotive repairs, and (5) automotive paint shops. Final reports of the individual waste audit studies will be available in Summer, 1987.

A second set of waste audit studies will target the following industries: (1) photographic processing laboratories, photographic finishing, and motion picture film processing; (2) commercial printing, letterpress and screen, engraving and etching; (3) educational, scientific, and research institutions; (4) general medicine and surgical hospitals excluding infectious wastes; and (5) fiberglass and reinforced molded or rigid plastic products including watercraft, electrical panels, figures, surfboards, and building panels. Contracts will be executed in Spring, 1987, with completion of the final reports in Fall, 1987.

WASTE MANAGEMENT INFORMATION TRANSFER

The objectives of this program are (1) to make industry more aware of economic, technical, and environmental advantages of waste reduction; (2) to establish credibility with industry that the State is available to assist them in the area of land disposal capacity and restrictions on land disposal of hazardous waste; and (3) to disseminate information and facts resulting from other components of the waste management program.

The Department has been accomplishing these objectives through seminars, fact sheets, reports, and by operation of the California Waste Exchange. The

Waste Exchange utilizes three major avenues to encourage recycling. A Directory Of Industrial Recyclers is published annually to inform generators about companies presently available to recycle their wastes. A Newsletter/Catalog is published on a triannual basis. More details about this activity are provided under the technology transfer component of the program which publicizes waste reduction opportunities or successful waste reduction projects. Staff also work directly with individual companies to assist them in recycling their waste.

Seminars provide a unique opportunity for industry, regulatory agencies, and the public to meet and discuss common goals, problems, and solutions. Seminars on specific waste management have been a successful strategy to expand awareness of the regulated community on waste reduction.

The first seminar series, fully funded and sponsored by the Department, involved Solvent Waste Management Alternatives. Two seminars were held in October, 1986; one in Los Angeles and the second in San Francisco. A final report entitled "Guide To Solvent Waste Reduction Alternatives" was prepared by ICF Consulting Associates, Inc. and presented to all 500 attendees. The focus of the study was on practical waste management alternatives to land disposal that have potential for reducing the amount and/or toxicity of solvent waste generated. Some of the major tasks performed included: (1) identification of major solvent-user industries in California; (2) a review of current waste management methods and technologies; and (3) characterizations of source reduction alternatives for minimizing solvent wastes, on-site and off-site solvent recycling treatment alternatives. A conference proceedings entitled "Solvent Waste Reduction Alternatives Symposia" was also prepared and is available.

A second symposium series designed to educate California's oil waste generators about alternatives to land disposal is scheduled for March, 1988, in Los Angeles and San Francisco. The study on which the symposium will be based, will be limited to oil wastes resulting from oil usage and can include lubricants, coolants, cutting and machining oils, and hydraulic fluids. A final report summarizing the results of the study and identifying the evaluation methods of managing oil wastes will be presented to each attendee. A conference proceedings will likewise be available after the symposium.

DEMONSTRATION STUDIES

EPA Funded Projects

The following projects are receiving direct funding through the EPA/DHS Cooperative Agreement. This element of the project will evaluate commercially available innovative alternative technologies for the treatment and on-site recycling of hazardous wastes. Each technology will be monitored and evaluated for treatment efficiencies and economic feasibility. Extent of funding ranges from $30,000 to $50,000. The projects are presented below.

California Agricultural Research will demonstrate the efficacy and economic feasibility of commercially available Aerobic Composting for the treatment of pesticide rinsewaters. The demonstration project will take place at the Chemical Waste Management Treatment Facility in Kettleman Hills, California, during the Spring of 1987.

The Department of Environmental Toxicology of the University of California, Davis will evaluate the treatment efficiency of an Oxidation/Ultraviolet Light System in conjunction with a biological treatment system for the degradation of pesticide rinseates. The project will occur at the U.C., Davis campus during the Spring and Summer of 1987.

Wesley M. Toy, P.E. will evaluate the efficacy and economic feasibility of an Evaporative Waste Concentrator for automotive repair wastes. The project will be performed in conjunction with Safeway Chemical in Saratoga, California in the Spring of 1987.

Roy F. Weston, Inc. will demontrate the treatment efficiency of a Low Temperature Thermal Treatment System for soils contaminated with volatile organic compounds. This process involves the stripping of volatile organic compounds (VOC's) from soils utilizing a recycling, low temperature oil system (300F). The demonstration project will take place at a site to be determined in the Spring/Summer of 1987.

Woodward-Clyde Consultants will evaluate the treatment efficiency of Ambersorb XE-340 as an alternative to granular activated carbon for the adsorption of chlorinated solvents from industrial waste stream. This project will be conducted in Cupertino, California in the Spring of 1987.

Ogden Environmental Services, Inc., who recently purchased GA Technologies circular combustion division, will monitor and evaluate a Circular Fluidized Bed Combustion Process to determine treatment efficiencies of cyanide and fluoride removal from aluminum spent potlining wastes. The project will occur in San Diego, CA in the Spring of 1987.

Hazardous Waste Reduction Grant Program

The California Waste Reduction Grant Program, established under Assembly Bill 685 (Farr) to promote innovative processes for managing hazardous wastes, is entering its second year. The Department seeks cost effective, practical strategies and technologies which would reduce the volume, mobility or toxicity of hazardous wastes. The Department awarded a total of $920,000 to 26 out of 97 applicants for fiscal year 85-86.

The major components of the projects funded were: (1) waste types which included waste oils, low heating value liquids and solids, pesticide rinsewaters, metals, chlorinated still bottoms, plating wastes and foundry sands; (2) technologies which included biological, chemical, & thermal treatment, recycling, freeze crystallization, mobile treatment, and oxidation; and (3) industries which included oil and gas refining, oil recycling, semiconductor manufacturing, pesticide application, aerospace, cast metals manufacturing, plating and electric utilities. Fifteen feasibility studies, including six for project designs, three for construction and demonstration, and two with public agency or university applicants were among the funded projects.

Based on the interest generated, the Department believes the program will be highly successful in demonstrating and evaluating waste reduction activities. The Department is now reviewing 106 grant proposals for the second year funding of $1,000,000.

CONCLUSIONS

Better knowledge in the areas of waste composition and volume, extent of treatment, and source reduction methods should make the California's hazardous waste management program more effective in the implementation of its ultimate goal, reduction of the volume of untreated waste being land disposed. New facilities and expansions of existing facilites will be needed to fully implement the ambitious goals of the federal and state statutes. Major efforts to overcome siting problems are needed to allow for the use of tested treatment alternatives. The State's hazardous waste management program is being continuously reviewed to assure that all its elements contribute as effectively as possible to the meeting of California's waste reduction goals.

FIELD ASSESSMENT OF STEAM STRIPPING VOLATILE ORGANICS FROM AQUEOUS WASTE STREAMS

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ABSTRACT

This paper discusses the removal of volatile organics (VO) from aqueous waste streams by steam stripping and summarizes the effectiveness of VO removal from the waste, the air emissions from the process, and the cost of the treatment process. Tests were conducted at two chemical plants that used continuous steam strippers to remove VO from the wastewater. The operation at Plant H, which produces ethylene dichloride and vinyl chloride monomer, treated about 852 liters per minute (L/min) or 225 gallons per minute (gal/min) of aqueous waste containing about 6 grams per liter (g/L) of VO. The operation at Plant I, which produces one-carbon chlorinated solvents, was smaller and treated 42 L/min (11 gal/min) of aqueous waste containing about 6 g/L of VO.

The test program evaluated the removal of VO from the water, which was about 99.8 to 99.999 percent at the two plants. At Plant H, the concentration of VO in the stripper bottoms ranged from 0.34 to 36 parts per million (ppm) with an average of 9.7 ppm. This wide range was caused by variations in the concentration of chloroform (the major constituent in the bottoms), which was apparently related to column fouling. This stripper processes wastewater containing about 1.4 g/L of filterable solids. At Plant I, the concentration of VO in the bottoms ranged from less than 0.005 to 0.13 ppm. Solids and an organic layer are removed in decanters at Plant I prior to steam stripping to provide a feed stream containing about 0.01 g/L of filterable solids. Emissions of VO from the decanter and storage tank vents at Plant I were estimated as 46 megagrams per year (Mg/yr). Significant vent rates of VO were also measured from the condensers at both sites. The condenser vent rate at Plant H averaged about 20 Mg/yr compared to 11 Mg/yr at Plant I. The condenser efficiency at Plant H ranged from an average of 6 percent for vinyl chloride to 99.5 percent for ethylene dichloride. At Plant I, the condenser efficiency ranged from 89 percent for chloromethane to 94 percent for chloroform.

INTRODUCTION

The EPA Office of Air Quality Planning and Standards (OAQPS) is currently developing regulations under the Resource Conservation and Recovery Act (RCRA) and its 1984 amendments to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). In support of this regulatory development effort, EPA's Hazardous Waste Engineering Research Laboratory (HWERL) is conducting field assessments of hazardous waste treatment processes that could be used to remove volatile organics (VO) from wastes. Volatile organics are defined as those organic compounds detected and quantified by EPA procedures, which include both purgeable and extractable compounds. Aqueous wastes represent a high percentage of the total volume of hazardous wastes. These aqueous wastes are often stored, treated, or disposed of in open area sources, such as surface impoundments and open wastewater treatment units, which are sometimes aerated. Steam stripping of the waste prior to placement in these open units is one promising technique that may reduce VO emissions from these sources.

APPROACH

This project focused on the use of continuous steam strippers. There are potential cost and cost-effectiveness advantages of continuous stripping, particularly for high volume aqueous wastes. Batch processes have been evaluated previously. The goals of the testing effort included measuring the effectiveness of the process for VO removal from the waste, measuring any air emissions, and assessing the cost of treatment. Samples of the feed stream to the steam strippers were taken for analysis by gas chromatography/mass spectroscopy (GC/MS) to identify purgeable and extractable organic compounds. No significant quantities of extractable organics were found at either plant; consequently, the sampling and analysis for each test focused on the purgeable organic compounds that were identified.

The sampling at each site was conducted over a 2-day period with 5 samples taken each day at about 2-hour intervals from each sampling point. The primary sampling points included the steam stripper's feed stream, bottoms, and condensate as shown in Figures 1 and 2. These liquid samples were collected in duplicate in 40 milliliter (mL) vials with no headspace. At Plant H, these samples were analyzed by EPA Method 624, which is a purge-and-trap procedure with analysis by GC/MS. The vapor flow rate and composition from the steam stripper's condenser system were also measured. At Plant H, the condenser/decanter was vented within a closed system to an incinerator. The system was maintained at a pressure of 1.3 atmospheres. The vapor flow rate in this closed system was measured by a tracer gas dilution technique. Propane was metered into the vapor inlet to the condenser at a known rate and the concentration of propane was measured downstream to calculate the vapor flow rate.

Samples of the wastewater from Plant I were screened by GC/MS to identify the organic compounds. Because only purgeable chlorinated compounds were found, EPA Method 601 was used for analysis of the samples from Plant I. At Plant I, the vapor flow rate from the condenser system was measured directly with a wet gas meter because the system was vented to the atmosphere. Vapor samples were collected in electropolished stainless steel canisters that had been previously cleaned and evacuated. The vapor flow rates and concentration measurements were used to calculate condenser efficiency. Additional liquid samples at each plant were taken for analysis of solids content, metals, pH, and VO in the headspace. Process data were collected for the steam stripping system and included flow rates and temperatures of the various streams entering and leaving the stripper.

The treatment system at Plant I also included removal of solids and any separate organic layer in decanters prior to steam stripping. Samples were taken from the streams entering and leaving the decanter for analysis of VO, solids, and metals to assess the effectiveness of the treatment and to determine the characteristics of residuals. In addition, vapor samples were taken from the headspace of the decanter and from the feed tank for the steam stripper to estimate air emissions.

PROCESS DESCRIPTION

The steam stripper at Plant H is used to treat wastewater from the production of ethylene dichloride and vinyl chloride monomer. At Plant I, the steam stripper is used to treat wastewater generated from the production of methylene chloride, carbon tetrachloride, and chloroform. The characteristics of the two waste streams are summarized in Table 1. The primary constituents at Plant H were ethylene dichloride (5,630 ppm) and chloroform (271 ppm). A total of 12 other compounds, mostly chlorinated organics, were also detected at Plant H at average levels that ranged from 0.3 ppm (for benzene) to 11 ppm (for 1,1-dichloroethane). At Plant I, methylene chloride (4,490 ppm) and chloroform (1,270 ppm) were the major constituents. A total of four additional chlorinated compounds were detected at average levels that ranged from 5.3 ppm (for 1,1,2-trichloroethane) to 55 ppm (for carbon tetrachloride). Total VO at both plants averaged about 6,000 ppm (6 g/L).

The stream stripper at Plant H used a tray column to treat water at a rate of about 852 L/min (225 gal/min). Solids at this plant were not removed prior to steam stripping and were processed through the steam stripper at a level of 1.4 g/L for filterable solids. Fouling of the heat exchanger and column from the accumulation of solids requires that this system be backflushed or cleaned periodically. The company prefers to process the solids through the steam stripper rather than install a system for solids removal. Removal of solids prior to steam stripping would generate a sludge that could be a hazardous waste requiring treatment before disposal. The vapors from the stripper pass through a primary condenser cooled with cooling tower water followed by a secondary condenser cooled with refrigerated glycol. Noncondensibles vented from the secondary condenser are routed to an incinerator. The condensate, which contains both an aqueous and organic phase, is recycled to the production process.

The steam stripper at Plant I was a packed column used to treat about 42 L/min (11 gal/min) of wastewater. The wastewater is treated for removal of solids and any separate organic phase in a decanter prior to stripping. The treatment includes pH adjustment, addition of flocculant, mixing, and settling for phase separation of each batch in the decanter over a 24-hour period. The aqueous phase is decanted and stored in the feed tank prior to steam stripping. Vapors from the steam stripper pass through a primary condenser and a secondary condenser, both cooled with cooling tower water. The condensate is separated in a decanter and the aqueous layer is returned to the column. The heavier organic layer is removed periodically and returned to the production process. The two solids decanters are also vented to the secondary condenser. The feed storage tank is vented to the atmosphere through a conservation vent.

After steam stripping, the wastewater from Plant H is sent to the wastewater treatment process, which includes solids removal and biological treatment. At Plant I, no additional treatment usually is needed (other than occasional pH adjustment) prior to discharge to the river.

VO REMOVAL FROM WATER

At Plant H, the removal of the major component (ethylene dichloride) was generally on the order of 99.999 percent with a feed concentration of 5,630 ppm reduced to 0.097 ppm in the stripper bottoms (see Table 1). The removal of chloroform averaged 99.6 percent for 6 of the 10 runs and averaged only 92.4 percent for the other 4 runs. A feed concentration of 271 ppm chloroform was reduced to an average in the bottoms of 9.6 ppm with a range of 0.13 to 36 ppm. The variations in chloroform removal appeared to be related to column fouling problems because the lowest values in the stripper bottoms were found after backflushing the steam stripper, and the highest levels were found before backflushing when the column pressure drop was increasing. None of the other 12 volatile compounds found in the feed at 0.3 to 11 ppm was detected in the stripper bottoms at a detection limit of 0.01 ppm. The percent removal for these compounds generally exceeded 99 percent. Total VO at this plant was reduced from an average feed concentration of about 6,000 ppm to an average of 9.8 ppm in the effluent, or about 99.8 percent removal of total VO.

The major constituent at Plant I (methylene chloride) was reduced from an average feed concentration of 4,490 ppm to 0.011 ppm (99.999 percent removal). Chloroform was reduced from 1,270 ppm to 0.006 ppm and carbon tetrachloride was reduced from 55 ppm to <0.005 ppm. The other chlorinated compounds present in the feed (chloromethane, trichloroethylene, and 1,1,2-trichloroethane) were not detected in the bottoms at a detection limit of 0.005 ppm. The total VO at this plant was reduced from about 6,000 ppm to <0.037 ppm with about 99.999 percent removal.

The removal efficiency of this steam stripper over the 2-day test was more consistent than that observed at Plant H. During the first test day, the levels of chloroform in the bottoms ranged from 7 to 9 ppb compared to all values $<$5 ppb on the second test day. None of the volatile compounds in the stripper bottoms exceeded 0.023 ppm for any of the samples.

CONDENSER EFFICIENCY AND AIR EMISSIONS

The condenser efficiency (Table 2) was evaluated at both plants from the quantity of VO entering the overhead system and the quantity leaving with the noncondensible gases. The condenser system at Plant H included two condensers in series that used cooling tower water followed by refrigerated glycol at 2 °C. A total of 7 of the 14 compounds detected in the feed were also detected and quantified in the vented vapors. The condenser removed 99.5 percent of the major constituent (ethylene dichloride) and about 96 percent of the chloroform. The removal efficiency for compounds present in lower concentrations was much lower. Vinyl chloride removal in the condenser averaged only 6 percent and indicated that this compound passed through the condenser in the vapor phase and was sent to the incinerator. The average flow rate from the condenser was 3.1 L/s and the total VO from the vent was about 20 Mg/yr (0.62 g/s). Although the condenser removed 99.5 percent of the ethylene dichloride from the vapor, ethylene dichloride was the major component of the vented vapors and comprised about one-half of the total VO vented to the incinerator.

The condenser system at Plant I also included two condensers in series; however, both were cooled with cooling tower water. Because of no significant differences in vapor phase concentrations and temperatures from samples taken after the two condensers, the small secondary condenser apparently was not removing any additional constituents. All of the significant condensation was provided by the primary condenser on the steam stripper. Vapor phase concentrations of VO after the primary condenser were high and averaged 44 percent VO by volume in the vapor phase or a mass concentration of 1.6 g/L at 25 °C. The vent rate was measured as 0.2 L/s. The condenser removed about 90 percent of the major constituent (methylene chloride) and about 94 percent of the chloroform from the vapors. The overall removal efficiency for total VO was approximately 91 percent. Emissions from the secondary condenser vent due to steam stripping were measured as 11 Mg/yr (0.34 g/s).

The vapor space in the solids decanter contained primarily methylene chloride (28 to 32 volume percent), chloroform (6.4 to 7.6 percent), carbon tetrachloride (1.5 to 3.8 percent), and chloromethane (0.6 to 1.0 percent). The vapor space in the feed tank also contained methylene chloride (9.7 to 12 percent), chloroform (2.5 to 3.1 percent), carbon tetrachloride (0.7 to 0.8 percent), and chloromethane (0.2 percent). Emissions from these two tanks were estimated based on the measured vapor phase concentrations and the working losses from the tanks based on a water transfer rate of 11 gal/min. Total VO emissions from the solids decanter were estimated as 35 Mg/yr or 1.7 grams per liter (g/L) of water treated. Total VO emissions from the feed tank were estimated as 11 Mg/yr or 0.5 g/L treated. The total VO emissions from the three major sources (condenser vent, solids decanter vent, and feed tank vent) were estimated as 57 Mg/yr or about 2.7 g/L treated. The estimate of annual emissions is based on an average water treatment rate of 11 gal/min for 50 weeks during a year.

Samples taken from the solids decanter showed that the treatment process could reduce filterable solids from 1,100 ppm to 50 ppm. Samples from the storage tank, which represented water decanted before our test, showed filterable solids levels of 11 ppm. Reductions in chromium, copper, nickel, lead, and zinc were also observed after treatment. Solids removal prior to steam stripping decreases column cleaning requirements and probably improves the consistency of the operation. However, the process generates about 190,000 L/yr of sludge, which contains the chlorinated compounds at levels of 20 to 30 percent. The solids removal process also increases the capital and operating cost of the treatment system. However, the bottoms from the steam stripper at this plant do not require any additional wastewater treatment (other than occasional pH adjustment) before discharge.

COST

Cost data were not available for the small steam stripper at Plant I. However, cost data were available for the steam stripper at Plant H and for a similar operation at Plant K, which treated a wastewater stream similar to that at Plant H. The steam stripper at Plant K was not evaluated in a full-scale test; however, process data, cost data, and samples were obtained during a one-day plant visit.

The basic process equipment for the steam stripping operation at Plant H includes a feed storage and surge tank, heat exchanger, the column and trays, two condensers in series, a decanter, 8 pumps, instrumentation, piping, and insulation. The total installed capital cost was estimated as $950,000 (1986 dollars). The major annual operating cost components include utilities (primarily steam), operating and maintenance labor, and laboratory support for analyses. A credit is included for the recovery of ethylene dichloride that is recycled to the production process. The annual operating cost was estimated as $250,000/yr. The total annualized cost, which includes capital recovery based on an interest rate of 10 percent and a lifetime of 10 years, was estimated as $405,000/yr or $0.89/1,000 L treated.

The data from the steam stripper at Plant H are compared in Table 3 with data obtained from a similar stripper at Plant K during a one-day plant visit. One difference between the two types is that the stripper at Plant H used trays for vapor/liquid contact whereas the Plant K operation uses a packed column. The basic feed constituents are similar; however, Plant K has a higher concentration of 1,2-dichloroethane in the feed. The difference in annual operating cost is probably attributable to the higher rate of steam usage at Plant K where approximately 75 percent of the annual operating cost is for steam. Both of these steam strippers achieve similar effluent (or bottoms) concentrations of VO in the range of 1 to 2 ppm. Although the steam usage for Plant K appears to be higher than that at Plant H, the steam rates in terms of VO removed are very similar (6.2 and 6.7 kg steam/kg VO removed). The small difference in cost effectiveness is probably not significant and can likely be attributed to the higher feed concentrations observed at Plant K.

Steam usage contributes significantly to the annual operating cost of a steam stripper. The steam usage at Plants I and K averaged about 0.1 kg/kg water treated compared to 0.036 kg/kg treated for Plant H. (Each of these plants used heat exchangers to preheat the stripper feed with the hot bottoms stream from the steam stripper.) These values compare favorably with some published design information on steam usage. Typical values of 0.07 to 0.24 (1), 0.1 to 0.3 (3), and 0.31 (2) kg steam/kg water treated have been reported.

CONCLUSIONS

Steam stripping can remove 99.8 to over 99.999 percent of the purgeable organic compounds found in the two waste streams. The presence of solids in the wastewater can lead to fouling problems and variations in performance; however, wastewater containing 1.4 g/L of filterable solids can be processed in a tray column steam stripper. When the condenser and tanks are vented to the atmosphere, emissions of 20 to 57 Mg/yr can result. The cost effectiveness of stripping a saturated wastewater stream in systems designed for 680 to 820 L/min was on the order of $120 to $220/Mg VO removed. The water treatment cost ranged from $0.89 to $1.57 per Mg or $3.38 to $5.96 per 1,000 gallons of water.

REFERENCES

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TABLE 1. SUMMARY OF AVERAGE STRIPPER FEED (IN) AND BOTTOMS (OUT) CONCENTRATIONS (ppm)[a]

	Plant H	
Constituent	In	Out
Ethylene dichloride	5,630	0.097
Chloroform	271	9.6
Benzene	0.27	<0.01
Carbon tetrachloride	1.7	<0.01
Chlorobenzene	0.38	<0.01
1,1-Dichloroethane	11	<0.01
1,1-Dichloroethene	4.7	<0.01
1,2-Dichloroethene	8.9	<0.01
Methylene chloride	1.2	<0.01
Tetrachloroethene	1.4	<0.01
1,1,2-Trichloroethane	7.5	<0.01
Trichloroethene	4.8	<0.01
Vinyl chloride	8.4	<0.01
Total	5,950	<9.8
Filterable solids (g/L)	1.4	0.93

	Plant I	
Constituent	In	Out
Methylene chloride	4,490	0.011
Chloroform	1,270	0.006
Carbon tetrachloride	55	<0.005
Chloromethane	33	<0.005
Trichloroethylene	5.6	<0.005
1,1,2-Trichloroethane	5.3	<0.005
Total	5,860	<0.037
Filterable solids (g/L)	0.011	0.009

[a] Averages of 10 samples taken over a 2-day test.

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TABLE 2. SUMMARY OF AVERAGE CONDENSER VENT RATES AND EFFICIENCIES

Plant H

Constituent	Condenser loading (g/s)	Vent rate (g/s)	Condenser efficiency (percent)
Vinyl chloride	0.089	0.084	6
Chloroethane	0.081	0.043	47
1,1-Dichloroethene	0.036	0.031	15
1,1-Dichloroethane	0.11	0.013	88
1,2-Dichloroethene	0.006	0.001	84
Chloroform	2.9	0.11	96
Ethylene dichloride	63	0.34	99.5
Total	66	0.62	99

Plant I

Constituent	Condenser loading (g/s)	Vent rate (g/s)	Condenser efficiency (percent)
Chloromethane	0.021	0.0024	89
Methylene chloride	2.9	0.29	90
Chloroform	0.81	0.045	94
Carbon tetrachloride	0.038	0.0039	90
Total	3.8	0.34	91

TABLE 3. COST COMPARISON

Item	Plant H	Plant K
Capital cost ($)	950,000	700 000
Operating cost ($/yr)	250,000	450,000
Total annualized cost ($/yr)[a]	405,000	564,000
Average feed rate (L/min)	820	680
Steam rate (kg/h)	1,790	4,090
Feed constituents (ppm)		
1,2-Dichloroethane	5,600	15,000[b]
Chloroform	270	17[b]
Other VO	59	31[b]
Bottoms constituents (ppm)		
1,2-Dichloroethane	0.16	.037[b]
Chloroform	0.8[c]	1.3[b]
Other VO	<0.01	1.4[b]
Steam usage		
kg/kg water	0.036	0.10
kg/kg VO removed	6.2	6.7
Cost-effectiveness		
$/Mg VO removed	220[d]	120[e]
$/1,000 L treated[f]	0.89	1.57

[a] Based on a 10-year lifetime at 10% (Capital recovery factor = 0.163).

[b] Based on a single sample analysis from presurvey trip.

[c] Based on 6 of 10 runs.

[d] Based on 1,820 Mg/yr recovered.

[e] Estimated from single analysis and 329 days/year operation.

[f] Also equals $/Mg treated.

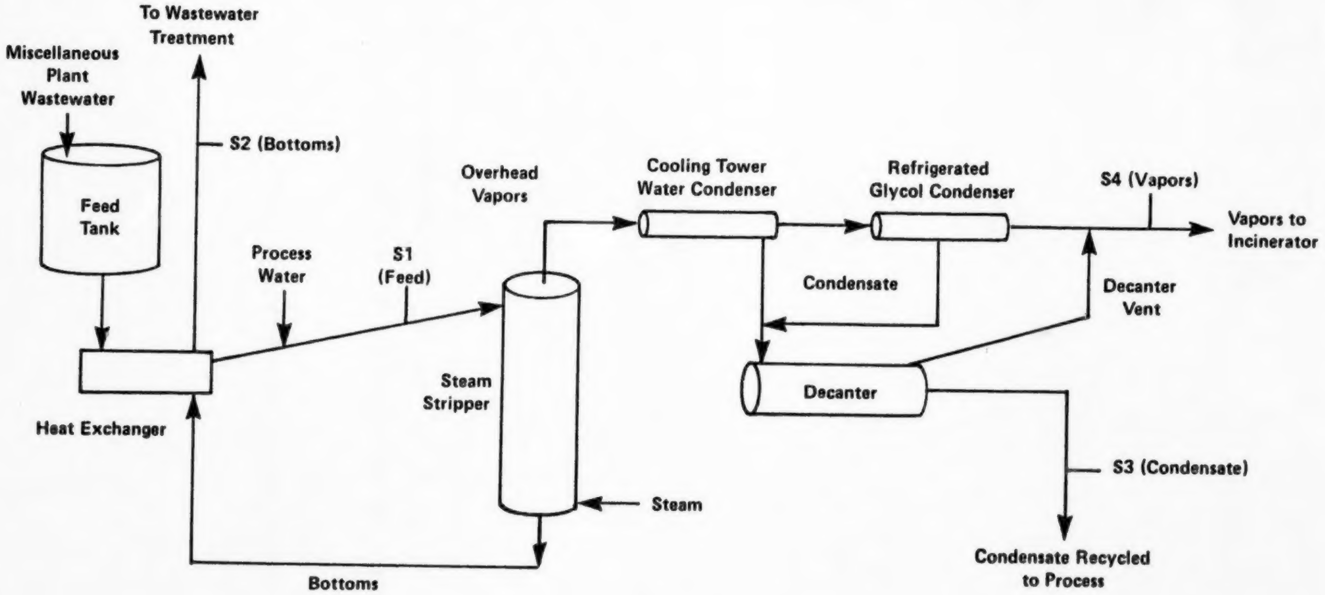
To Wastewater Treatment
Miscellaneous Plant Wastewater
Feed Tank
S2 (Bottoms)
Heat Exchanger
Process Water
S1 (Feed)
Overhead Vapors
Steam Stripper
Steam
Bottoms
Cooling Tower Water Condenser
Refrigerated Glycol Condenser
Condensate
Decanter
S4 (Vapors)
Vapors to Incinerator
Decanter Vent
S3 (Condensate)
Condensate Recycled to Process

Figure 1. Schematic of steam stripper and sampling locations for Plant H. (S = sampling point).

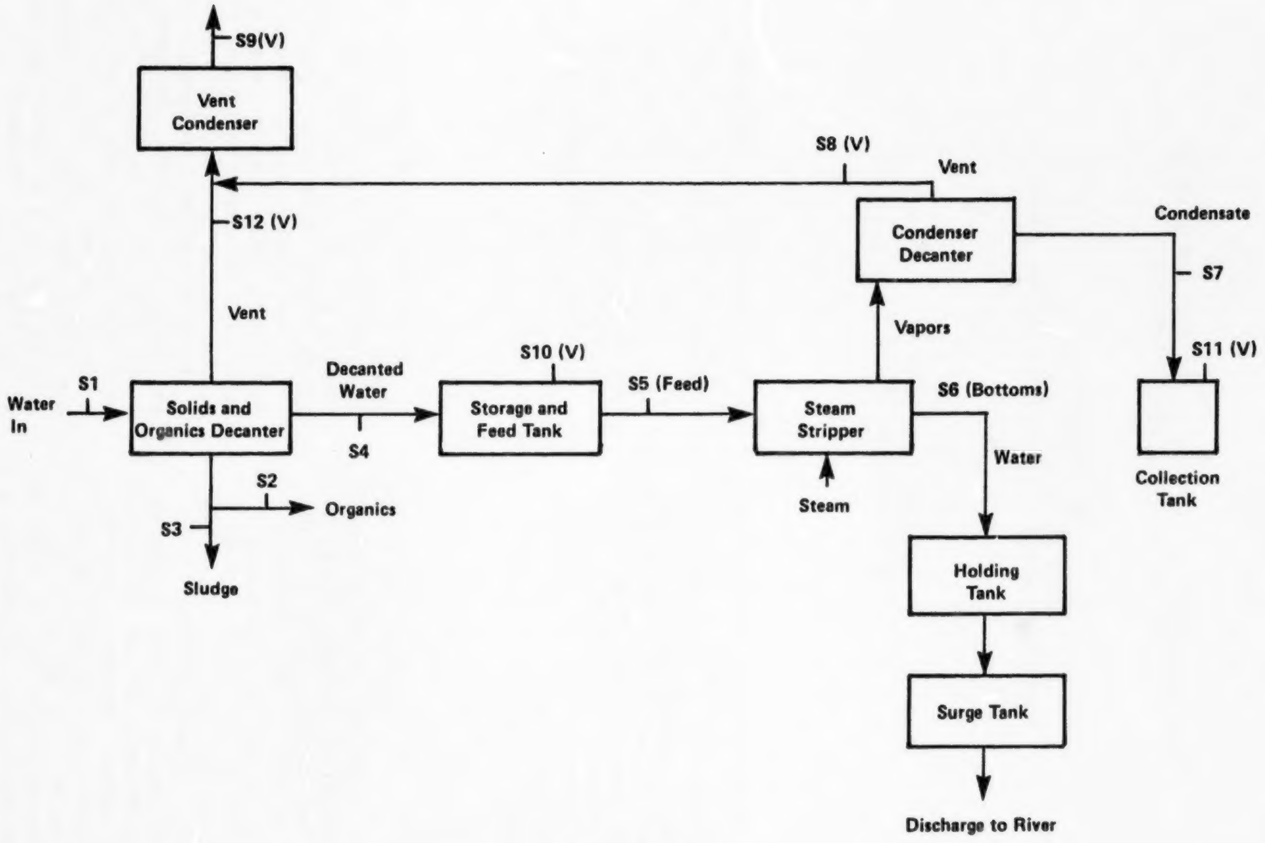
S9(V)
Vent Condenser
S8 (V)
Vent
S12 (V)
Condenser Decanter
Condensate
S7
Vent
Vapors
S11 (V)
S10 (V)
Decanted Water
S5 (Feed)
S6 (Bottoms)
S1
Water In
Solids and Organics Decanter
S4
Storage and Feed Tank
Steam Stripper
Water
Collection Tank
S2
Organics
Steam
S3
Sludge
Holding Tank
Surge Tank
Discharge to River

Figure 2. Simplified schematic of sampling points for Plant I.
(S = sampling point, V = vapor sample)

FIELD ASSESSMENT OF THE FATE OF VOLATILE ORGANICS IN AERATED WASTE TREATMENT SYSTEMS

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ABSTRACT

Aeration of wastewater containing volatile organic compounds in activated sludge systems effectively removes many of these compounds from the wastewater prior to discharge. Studies were conducted at a full-scale treatment systems to determine the relative extent to which various compounds were destroyed biologically and stripped into the air. Direct measurements of air emissions were made through sampling and chemical analysis of off-gases from the aeration tank of an activated sludge unit. Indirect measurements were made by comparing compound specific biological oxidation rates obtained in closed bottles to total disappearances across the treatment units. Additional measurements were made to determine potential removal of organics in waste sludge streams. This paper describes these measurement techniques and results of the studies.

INTRODUCTION

Industrial wastewater is often treated in aerated biological oxidation units to remove dissolved organic chemicals prior to discharge or reuse. For relatively dilute streams containing biodegradable compounds, treatment processes such as activated sludge are typically effective and economical. Organic material is removed from wastewater in these processes by aerobic organisms which use the material as a food source. Oxygen is supplied to the organisms either by bubbling air through the wastewater, agitating the surface of the wastewater or some combination of these mechanisms. In addition to supplying oxygen to the organisms responsible for biodegradation, the aeration is necessary to keep the biomass suspended and to provide adequate mixing.

When volatile and semivolatile compounds are present in the wastewater which is aerated, the possibility exists that some or all of the removal of these compounds results from mass transfer to the air rather than biological decomposition. In order to determine the relative importance of these mechanisms, the total removal in the unit must be determined and a direct or indirect measurement of air emissions must be made. An indirect measurement of air emissions can be made by determining the rate of biooxidation in a closed system where mass transfer to the air is not significant, and comparing this rate to the total disappearance measured across the actual treatment unit. Direct air emissions measurements can be made by sampling and analyzing air over the aeration tank in a way that permits an accurate calculation of the flux from the aeration tank. The accuracy of either direct or indirect methods depends on the capability of the technique to monitor the physical or biochemical process without significantly affecting the rate. The accuracy of chemical analyses of gas or liquid samples is also crucial to the accuracy of the overall measurement.

This study was done as part of a project to support efforts by the EPA Office of Air Quality, Planning, and Standards to estimate air emissions from specific treatment processes. An understanding of the potential magnitude of emissions of this type is required for development of national emissions models in support of regulations under the Resources Conservation and Recovery Act. The major objectives of this field test were to obtain direct measurements of air emissions from a submerged aeration activated sludge tank using an isolation mass flux chamber at various locations on the tank surface, and to also measure compound specific biodegradation rates and total removals in the activated sludge tank so that a calculation of air emissions could be made by difference. In addition, process operating conditions which affect both biochemical and physical removal were monitored.

At the outset of the project, it was hoped that a comparison between the direct and indirect measurement techniques could be made on a compound-specific basis. A confirmation of the indirect measurements by the direct measurement technique would support use of the indirect technique at surface aerated facilities where direct air measurements are more difficult. Analytical limitations precluded this comparison at this site except for the compound, 1,1,1-trichloroethane. The phenolic compounds determined by EPA priority pollutant methods in liquid samples were not quantifiable with the gas phase analytical system used in this study.

Minor objectives of the field test included determination of overall removals of specific organic compounds from the wastewater treatment system as a whole and determination of experimentally measured air/water and water/biomass solids partition coefficients for use in generic evaluations of similar systems. The test was conducted by Research Triangle Institute (RTI) and Radian Corporation. RTI had primary responsibility for liquid sampling and analysis, total removal calculations, air/water and water/biomass solids partition coefficients, and compound specific biodegradation rate determinations. Radian had primary responsibility for air sampling and analysis and direct air emissions calculations. Sampling was conducted between September 22 and September 26, 1986.

TEST DESCRIPTION

At the facility tested, wastewater is collected at various points in the manufacturing area of the plant and pumped intermittently to a sump in the wastewater treatment area. Wastewater is pumped intermittently from this sump to an equalization tank with a residence time of approximately 90 hours. The equalization tank is not completely mixed and is operated primarily to accommodate hydraulic surges.

Wastewater is then pumped to a splitter box where it is mixed with recycled sludge and divided between two identical parallel above-ground concrete aeration tanks providing approximately six days residence time. Air is supplied through static mixers in each tank. Approximately two inches of foam was present on the surface of the tanks except in the areas directly above the mixers. The aeration tanks contained 2,500 mg/L of mixed liquor suspended solids during the test. The water level is maintained by an overflow weir.

The wastewater from the two tanks overflows to a splitter box where it is recombined and then divided evenly between two clarifiers. Sludge is returned to the aeration tanks at the influent splitter box in an amount sufficient to maintain the desired volatile suspended solids content of the mixed liquor.

AIR SAMPLING

The tank was divided into twenty-seven 2.44 m x 2.44 m grids. An enclosure device, the isolation emission flux chamber (see Figure 1), was used to measure the off-gas flow rate from the different parts of a grid. A slipstream of the sample gas was collected for hydrocarbon analysis.

The first day and a half of sampling was used to assess the spatial variability of a grid in terms of VOC emissions and air flow rate. To accomplish this, flow rate measurements and THC concentration measurements were made at various grid points and locations within the grids. Only the on-site total hydrocarbon analysis was performed for samples collected on the first days of sampling. Based upon this preliminary work, the tank was divided into three zones, directly above the aerators (A), foam covered (C), and non-aerated (NA). These zones are shown schematically in Figure 2.

The order of sampling was randomly determined, with 18 grid points (six per zone) being sampled over the following two-day period. At each location, a gas sample was collected for on-site methane, and total non-methane hydrocarbons (TNMHC) and screening-level compound analysis, and a second gas sample was collected for detailed speciation at Radian's Austin laboratories. A total of 20 stainless steel canister samples (including duplicates) and a canister blank were collected over the two-day sampling period. Two liquid samples were collected in VOA vials at each of the eighteen sampling points. The total air flow rate to the tank was determined by using the fan performance curve (amperes vs. air flow rate) and amperage data continuously recorded on a stripchart recorder during the site investigation.

The air sampling approach chosen used an enclosure device, referred to as an emission isolation flux chamber, to sample gaseous emissions from a 0.13 m^2 surface area. A pump was used to withdraw sample gas from the flux chamber at the same rate at which it entered. This was confirmed by monitoring the pressure in the chamber. The volumetric flow rate of air through the chamber was recorded and the concentration of the species of interest was measured at the exit of the chamber. The emission rate was calculated as:

$$E.R._i = \frac{(C_i)(Q)}{A} \qquad (1)$$

where: $E.R._i$ = emission rate of species, i ($\mu g/m^2 min$),
C_i = measured concentrations of species i (ppmv converted to $\mu g/L$),
Q = air flow rate (L/min), and
A = exposed surface area (m^2).

The chamber (see Figure 1) is an acrylic dome with a lower ring-shaped stainless steel section. The chamber has a 0.130 m^2 exposed surface area and a volume of approximately 0.03 m^3 (when immersed to a depth of 1 inch). One 0.019 m (3/4-inch) diameter port was used to withdraw sample gas. All other ports were sealed. A flotation system, consisting of three circular pontoons attached to telescoping legs, was connected to the flux chamber for buoyancy control.

LIQUID SAMPLES

Samples of equalization tank influent, aeration tank feed, aeration tank effluent, recycled sludge and clarifier overflow were taken. In addition, samples of the mixed aeration tank feed/recycled sludge influent to the aeration tank were taken for biodegradation rate testing. Samples of actual mixed liquor taken by Radian for correlation with flux chamber measurements were provided to RTI for analysis.

Samples of the mixed feed to the aeration tank were dipped from the influent splitter box at the entrance to the aeration tank with a four gallon plastic bucket. This volume formed the gross sample for biodegradation rate studies.

The liquid samples were analyzed for acid extractable organic priority pollutants by EPA Method 625 and for purgeable organic priority pollutants by EPA Method 624. In addition to those compounds specified in the methods, the mass spectra were compared to a library of compounds, identifications and quantitations were made based on spectral comparisons.

A limited number of samples were analyzed for methanol by direct aqueous injection gas chromatography with a flame ionization detector. Dissolved oxygen measurements were made in situ using a YSI dissolved oxygen meter with a membrane electrode. Volatile suspended solids analyses of aeration tank effluent, recycle sludge, and influent splitter box samples corresponding to biodegradation rate determination samples were conducted by Standard Method 209E. Volatile suspended solids data were supplemented with data supplied by plant personnel determined using the same method. Chemical oxygen demand data were obtained from plant records.

BIODEGRADATION RATE TESTING

In order to distinguish between removal of organics from mixed liquor due to biodegradation and removal due to mass transfer into the air, experiments were conducted which permitted biodegradation to take place while limiting air stripping. Samples of a mixture of aeration tank feed and recycled sludge were dipped from the influent splitter box at the upstream end of the aeration tank.

Each sample was divided using a two liter Nalgene graduated cylinder as follows: up to seven, one liter bottles were partially filled with 500 mL of mixture, one one-liter bottle was completely filled with mixture, and one specially prepared 500 mL bottle was partially filled with 250 mL of mixture. The filled bottle was designated for volatile suspended solids analysis and immediately stored on ice. One of the partially filled one liter bottles was immediately preserved with 10 mL of saturated copper sulfate solution and agitated gently to assure that the copper sulfate solution was distributed. This bottle was then used to fill two 40 mL septum vials. The one liter bottle and the two 40 mL bottles were stored on ice immediately thereafter for shipment to a laboratory for organic compound analysis.

The specially prepared 500 mL bottle had a plastic tubing stub fitted into and protruding through the cap. Tygon tubing was connected to the stub leading to a plastic T-connector. One side of the T-connector was attached to a short length of tubing filled with lithium hydroxide. The other side of the T-connector was connected to a mercury manometer. This bottle was used to monitor oxygen uptake over time.

The partially filled one liter bottles and the partially filled 500 mL bottle were then mounted on a wrist action shaker and continuously agitated. Over a period of about 19 hours, bottles were removed from the shaker, one by one and preserved with copper sulfate using the same procedure as for the initial sample. Similarly, 40 mL vials were filled for purgeable organics analysis.

Biodegradation rate test samples were analyzed for purgeable organics, acid extractable priority pollutants, and methanol. A total of four tests were conducted, with two tests run simultaneously from the same sample of aeration tank feed/recycle sludge mixture.

The total oxygen uptake within the specially prepared bottle was monitored to insure that the oxygen within the headspace was not exhausted. When the oxygen in the headspace was approximately 50% of that initially present, the bottles remaining on the shaker were vented and fresh air was allowed to replace that initially present. This was done once in the course of the experiment.

RESULTS

Direct Air Emissions Measurements

Compound specific emissions rates are given in Table 1. Methane emissions were larger than those of any class of compound. The TNMHC emitted from the lagoon was much less than 1 kg/day. Emissions were highest for Zone C (foam covered areas) in all cases except in the case of the insignificant amount of sulfur species and unidentified VOs emitted. Zone A (directly above the aerators) emissions are generally less than Zone C reflecting the smaller total area of Zone A. It is probable that sufficient air is present in Zone A to strip out all VOs and that any excess air merely acts to dilute the off-gas.

These values have been corrected for the blank sample values and for a sampling bias at low flow rate. The total air flow rate based on the fan curve was 15 m^3/min.

The spatial variabilities observed were not expected and indicate that the subsurface flow patterns or the emission processes are not fully understood. The large methane emissions from the aerated zone imply either a non-biological origin or production outside the aerated zone.

Indirect Measurements

Typical biodegradation test data are shown in Figure 3. The slope of the linear regression line through the data points represents the best estimate of the compound specific biodegradation rate. Concentrations would be expected to decline monotonically in the absence of chemical analysis errors. This slope was then normalized for the biomass concentration. Selected biodegradation rate constants are given in Table 3. Multiple rates for the same compound reflect data obtained during different tests. Taking the rate constant for phenol, as an example, as 0.25 μg/min g biomass, would imply that a tank with a six day residence time, operated with mixed liquor volatile suspended solids of 2500 mg/L could effectively biodegrade 5400 μg/L of phenol. The actual difference between phenol in the influent and the effluent of the aeration tank during the study period averaged 6200 μg/L (based on a weighted average of aeration tank feed concentration and recycled sludge vs. aeration tank effluent. the effluent and recycle streams were below the detection limit of 250 μg/L). Based on this rate, 86% of the phenol removed in the system was biodegraded and 14% was emitted to the air. The uncertainty in the rate calculation is great enough that all of the phenol removed may be due to biodegradation, as the coefficient of variation of the biodegradation rate varied between 90% and 200%. The rate for 2,4,6-trichlorophenol, 0.037 ± 47% μg/min-gram biomass, indicates that approximately 800 μg/L of this compound could be biodegraded in this system. The average aeration tank influent concentration (feed plus recycled sludge) was approximately 1900 μg/L; aeration tank effluent concentration was consistently below the detection limit of 250 μg/L. Potential air emissions of 2,4,6-trichlorophenol may be as great as 58% of the influent.

The biodegradation rate for 1,1,1-trichloroethane was essentially zero. This compound was detected in the direct air samples taken with the flux chamber at 1,330 μg/min, but this was much less than the mass in the aeration tank influent (10,000 μg/L). The difference is either due to failure to detect the biodegradation of this compound (perhaps by not continuing the test long enough) or else to incomplete capture in the flux chamber.

A similar calculation for 1,1,1-trichloroethane indicates that most of the difference in concentration between influent and effluent could be due to volatilization.

Water/biomass solids partition coefficients are given in Table 3.

CONCLUSIONS

The results of this field test did not confirm the suitability of the indirect air emissions estimation approach. The major reason for this was that chemical limitations prevented, for the most part, analysis of the same compounds in both the liquid and gaseous streams. Direct air emissions measurements of a number of compounds were obtained and can be correlated with influent concentrations. Similarly, biodegradation rate estimates and water/biomass solids partition coefficients were experimentally obtained for use in the absence of more accurate site-specific data.

TABLE 1. TOTAL EMISSIONS FOR SELECTED INDIVIDUAL COMPOUNDS

Compound	Total emissions (μg/min)			
	Aerated Zone A	Foam covered Zone C	Non-aerated Zone NA	Total Tank
Methane	50,000 ± 22,600	263,000 ± 50,700	2,080 ± 11,600	316,000
C-2 VOC	287 ± 236	1,800 ± 571	-55.6 ± 81.2*	2,040
Cyclopentane	696 ± 555	1,040 ± 1,520	26.8 ± 77.3	1,770
Isobutene + 1-Butene	62.3 ± 89.6	187 ± 220	-15.5 ± 28.3*	234
t-4-Methyl-2-Pentene	105 ± 93.2	80.0 ± 85.3	17.7 ± 62.4	202
Toluene	114 ± 1,120	6,100 ± 10,300	-630 ± 1,780*	5,570
Methylene chloride	161 ± 149	153 ± 269	-73.3 ± 29.9*	241
1,1,1-Trichloroethane	385 ± 166	934 ± 795	10.2 ± 44.5	1,330
Acetaldehyde	5,480 ± 1,930	5,350 ± 2,320	-213 ± 262*	10,600
Acetone	7.71 ± 298	159 ± 874	-278 ± 51.9*	-111*
Dimethylsulfide	127 ± 70.6	112 ± 78.7	0.00 ± 0.0	239 ± 124
Total Air Flux (m^3/min)	18.6	25.4	3.85	47.9

*Negative emissions result from correction for blank.

TABLE 2. BIODEGRADATION RATE CONSTANTS

Compound	Rate Constant µg/(min-g biomass) ± 1 S.D.
Methanol	12.8 ± 38 percent 5.7 ± 54 percent
Phenol	0.087 ± 150 percent 0.25 ± 91 percent 0.29 ± 200 percent
2,4,6-Trichlorophenol	0.037 ± 47 percent
Styrene	0.0011 ± 123 percent
Oxirane	0.38 ± 56 percent 0.59 ± 47 percent
1,1,1-Trichloroethane	0

TABLE 3. SLUDGE/WATER PARTITION COEFFICIENTS

Compound	Recycle [(µg/kg)/(µg/L)]	Effluent [(µg/kg)/(µg/L)]
Methylene chloride	140	NM
Oxirane	170	69
2-Propanone	160	57
2-Propanol	170	130
1,3-Dioxolane-2-methanol	170	140
Dimethyl disulfide	150	NM

NM = Not meaningful (samples below detection level).

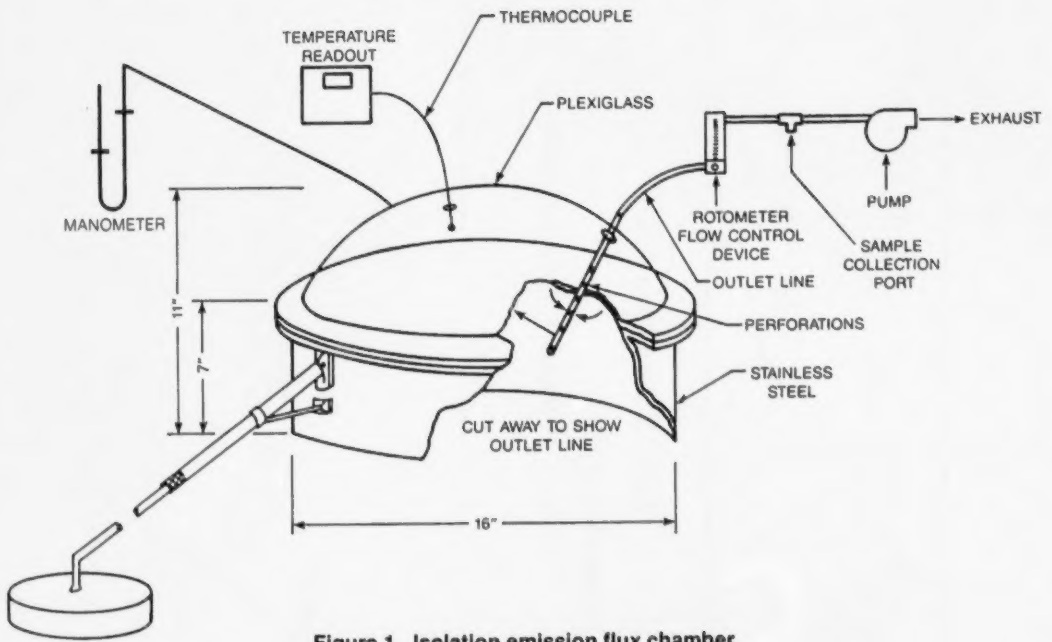
THERMOCOUPLE
TEMPERATURE READOUT
PLEXIGLASS
EXHAUST
MANOMETER
PUMP
ROTOMETER FLOW CONTROL DEVICE
SAMPLE COLLECTION PORT
OUTLET LINE
PERFORATIONS
11"
7"
STAINLESS STEEL
CUT AWAY TO SHOW OUTLET LINE
16"

Figure 1. Isolation emission flux chamber.

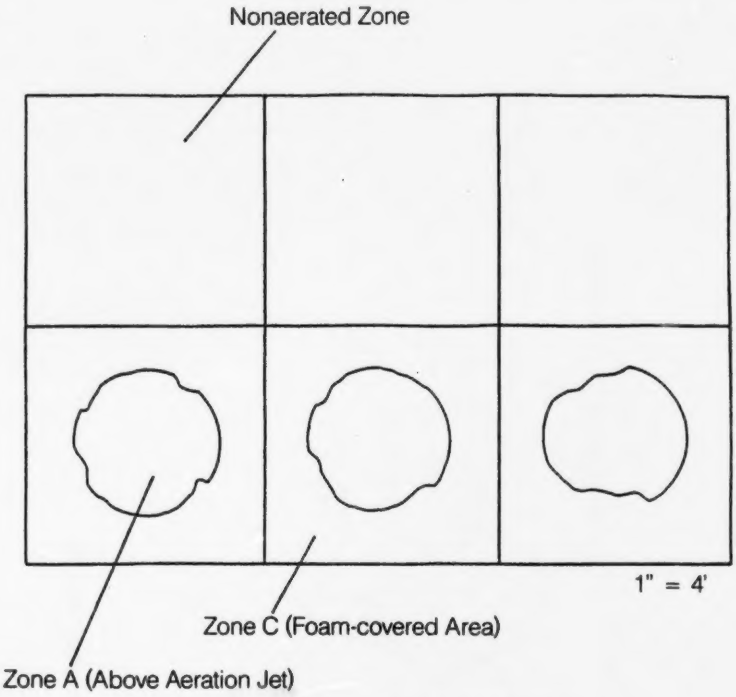
Nonaerated Zone
1" = 4'
Zone C (Foam-covered Area)
Zone A (Above Aeration Jet)

Figure 2. Aeration tank zone designations.

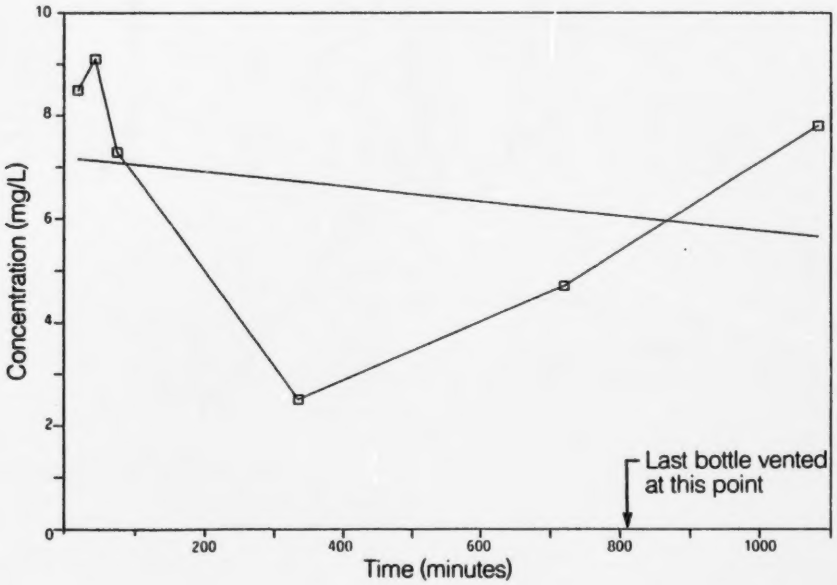

Figure 3. Concentration of phenol in biodegradation rate test samples.

PILOT-SCALE EVALUATION OF A THIN-FILM EVAPORATOR FOR VOLATILE ORGANIC REMOVAL FROM LAND TREATMENT SLUDGES

by

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ABSTRACT

The U.S. Environmental Protection Agency Office of Air Quality Planning and Standards is currently developing regulations to control air emissions from waste treatment, storage, and disposal facilities. In support of this regulatory development effort, the Research Triangle Institute has conducted a study of thin-film evaporators (TFE) for removing volatile organics (VO) from refinery wastes. Thin-film evaporators were studied to evaluate their use to remove and recover VO from waste petroleum sludges prior to land treatment. This would reduce the amount of VO available for release to the atmosphere during land treatment of the sludges.

The treatment of two refinery sludges was investigated in a pilot-scale agitated TFE. The fraction of feed removed by the TFE ranged from 11 to 95.7 percent. At the greatest overhead fraction, more than 99.9 percent of the VO and 75 percent of the semivolatile compounds were removed from the sludge. At the lowest overhead fraction, greater than 98.5 percent of the VO and 10 to 43 percent of the semivolatiles were removed from the sludge. The sludge processed with the lowest overhead fraction contained water and maintained suitable handling characteristics for land treatment.

INTRODUCTION

The TFE test was conducted at Luwa Corporation in Charlotte, NC, during the week of September 8-12, 1986. Due to regulatory constraints, the wastes that were tested were nonhazardous (as defined by RCRA) refinery wastes. These wastes were selected based on their similarity to hazardous refinery wastes, such as API separator sludge (hazardous waste code K051), that are currently land-treated.

The use of TFEs was investigated to determine if VO can be removed and recovered from waste petroleum sludges prior to land treatment of the sludge. This would reduce the amount of VO available for release to the atmosphere during land treatment of the sludges. The VO would be recovered as an organic condensate and recycled to petroleum refineries as product. In addition to VO removal, the process can also be operated to remove water and low boiling oils from sludges, reducing sludge volume while recovering oil from sludges prior to disposal. These benefits are not limited to sludges disposed of by land treatment.

THIN-FILM EVAPORATION

Agitated TFEs are designed to spread a thin layer of viscous liquids or sludges on one side of a metallic surface with heat supplied to the other side. This promotes the transfer of heat to the material while simultaneously exposing a large surface for evaporation of volatile compounds. Heat can be supplied by either steam or heated oil; heated oils are used to heat the waste to temperatures higher than can be achieved with saturated steam. Volatile constituents separate from the feed liquid or sludge, producing a vapor stream of volatiles and leaving a treated waste which flows out of the bottom of the evaporator. Vapors can be condensed and recovered.

The unique feature of this equipment is not the thin film itself (falling- and rising-film evaporators use thin liquid layers), but rather the mechanical agitator device for producing and agitating the film. This mechanical agitator permits the processing of high-viscosity liquids and sludges with suspended solids. The agitation at the heat transfer surface not only promotes heat transfer but also maintains precipitated or crystallized solids in manageable suspension without fouling the heat transfer surface.

With typical tip speeds of 900 to 1,200 cm/s (30 to 40 ft/s), centrifugal forces distribute the feed as a thin film on the heated cylinder wall, and the wave action produced by the rotating blades provides rapid mixing and frequent surface regeneration of the thin liquid layer on the transfer surface. A typical vertical thin-film evaporator is illustrated in Figure 1.

PILOT FACILITY AND TEST

The tests were conducted at the pilot facility of Luwa Corporation, Charlotte, NC. This facility contains a variety of evaporators produced by the company and is used to test potential applications of their equipment for clients. The equipment used for the tests was judged most suitable for our applications. Samples of tank bottoms sludges were obtained from an oil refinery, tested in the equipment, and then returned to the refinery for normal disposal.

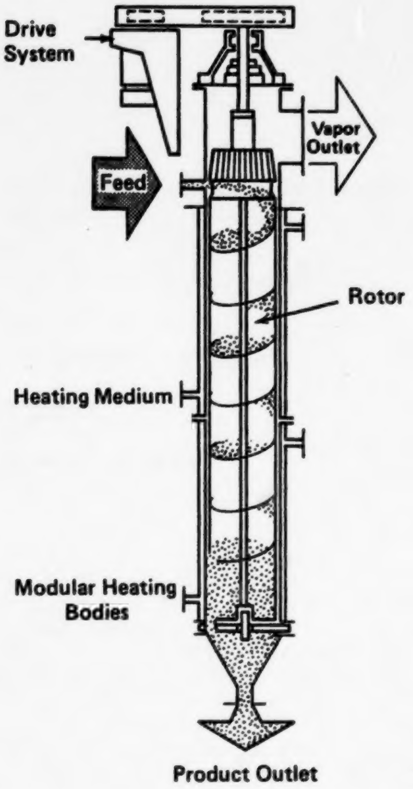

Figure 1. Luwa vertical thin-film evaporator.

Figure 2 shows the equipment used in the pilot-scale tests. The 100-gal feed tank was agitated with both an axial mixer and continuous recirculation of the feed liquid through a centrifugal pump. A positive displacement pump was used to pump the feed sludge through the preheater and into the top of the TFE. There, the sludge was continuously spread over the heated surface of the TFE. Unevaporated material flowed down through the TFE to a collection pot at the base. Materials evaporating in the TFE passed through an empty demister and were condensed in a condenser that was cooled with cooling tower water. Condensate flowed from the condenser and was collected directly into liquid sample jars or a flask used for measuring condensate volumes. Any uncondensed vapors flowed from the condenser through a wet testmeter for flow measurement.

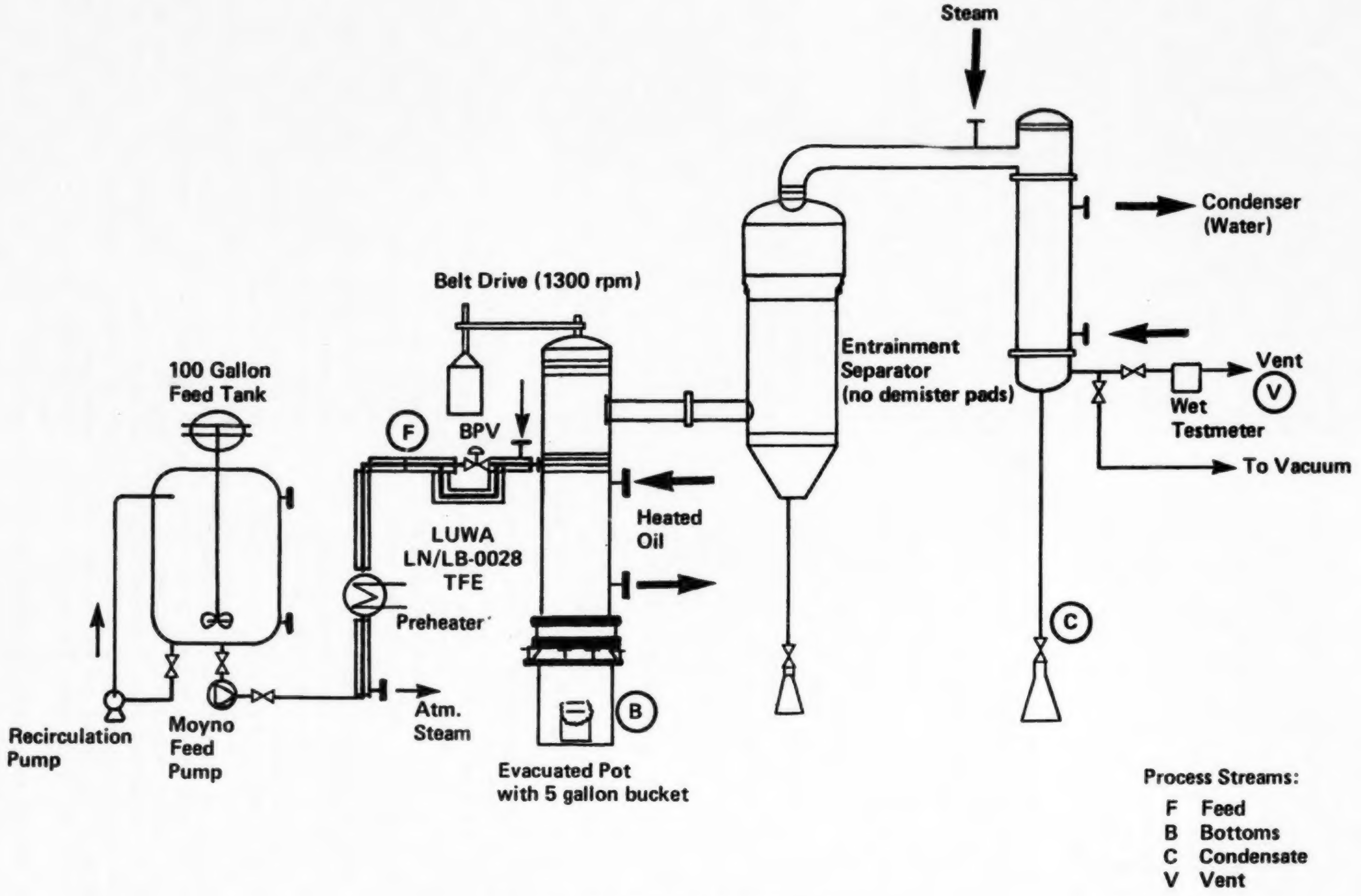
Steam
Condenser
(Water)
Belt Drive (1300 rpm)
Entrainment
Separator
(no demister pads)
Vent
V
Wet
Testmeter
To Vacuum
100 Gallon
Feed Tank
F
BPV
LUWA
LN/LB-0028
TFE
Heated
Oil
Preheater
C
B
Recirculation
Pump
Moyno
Feed
Pump
Atm.
Steam
Evacuated Pot
with 5 gallon bucket
Process Streams:
F Feed
B Bottoms
C Condensate
V Vent

Figure 2. Configuration of test equipment.

The TFE was heated by hot oil, although steam could be used for lower temperatures. Entrainment separators are used frequently with TFEs to remove entrained liquids from the vapors flowing to the condenser. The entrainment separator was empty (but heated) during the testing, and very little material condensed there. Five feed lines from the preheater to the TFE were heated with low-pressure steam, as were the vapor lines from the TFE through the entrainment separator and to the condenser.

A total of 22 runs were performed with the TFE, using two different wastes, three temperatures, three flow rates, and under both atmospheric and vacuum operation. The feed rates and temperatures were chosen to operate the TFE over its normal range of operation and to demonstrate the removal of VO compounds from the feed sludges. Tests 1 through 18 used five 55-gal drums of an emulsion tank sludge while tests 19 through 22 were performed on oily tank bottoms. The process testing, sampling, and analysis concentrated on the tests using the first waste while the second waste was used to gather additional process data and demonstrate process operation on a second waste sludge.

Matrices indicating operating conditions and run numbers for the tests are shown in Table 1. This test plan studied the two major variables affecting TFE performance, the temperature of the heating jacket and the feed rate. The indicated flows and temperatures were the nominal process parameters during the tests and the actual measured parameters varied somewhat from these values. Runs 5, 6, and 7 were a series of tests at a constant heating jacket temperature (150 °C) at three different feed rates. Runs 8, 9, and 10 were conducted at similar flow rates to Runs 5, 6, and 7 but were at a much higher heating jacket temperature (310 °C). Runs 14, 15, and 16 were conducted at an intermediate temperature (230 °C) and were limited to the two lower flow rates. Runs 1-4, 12, and 13 were used as shakedown runs. These runs allowed practice samples to be taken and potential problems to be solved before the samples to be analyzed were taken.

Three vacuum runs were performed with the first waste sludge during Runs 11, 17, and 18. The purpose of these runs was to examine the effect of vacuum operation on the removal of VO compounds from the feed waste. The final four runs (19, 20, 21, and 22) were performed with the second waste. These tests were principally to demonstrate the operation of the TFE with a second waste sample and were not extensively sampled and analyzed during the project.

Four of the tests (5, 7, 8, and 10) were selected for extensive sampling and analysis of process streams. These four runs allowed the process to be examined with both high and low feed rates and at both high and low heating temperatures. They represent the range of reasonable operating conditions for the TFE processing waste sludges for the removal of volatiles, water, and oils from the sludge.

SAMPLING AND ANALYSIS

Samples were taken to characterize the wastes treated during the pilot studies and to determine the efficiency of the TFE process. Four process streams were sampled: feed, bottoms, condensate, and condenser vent gas. The procedures for obtaining these samples are outlined in a specific test and quality assurance plan. In all cases, special precautions were taken to obtain representative samples and to prevent the loss of VO from the samples prior to analyses.

Sample analysis was performed onsite by RTI and offsite by contract laboratories. The onsite measurements performed by RTI were: (1) the analysis of headspace concentrations of VO from feed sludge samples and bottoms samples and (2) the measurement of vent gas flow rates and overall VO concentrations in the vent gas and bottoms collection pot. Two types of analyses for headspace concentrations of VO were employed. The first used syringes to transfer gas samples from half-filled sample bottles and a portable GC to measure the concentrations of VO in air above the samples. The second method of measuring the headspace concentrations of VO used a calibrated total hydrocarbon analyzer. This instrument was a Bacharach TLV Sniffer that pulls a continuous sample that is continuously oxidized by a catalyst-coated resistance element. The resistance of this element varies with

TABLE 1. THIN-FILM EVAPORATOR TEST PLAN

Feed No. 1, Emulsion Tank Bottoms

Flow Rate (lb/hr)	Temperature (°C) 150	 230	 310
70	Run 5	Run 14	Run 8
100	Run 6	Run 15 Run 16	Run 9
150	Run 7		Run 10

Feed No. 2, Oily Tank Bottoms

Flow Rate (lb/hr)	Temperature (°C) 150	 310
45	Run 21	Run 19
80	Run 22	Run 20

temperature, which is in turn proportional to the hydrocarbon concentration of the analyzed gas. These measurements were intended to be a rough analysis of headspace concentrations and to confirm the results from GC analysis. The Bacharach TLV Sniffer had a maximum measurable concentration of 10,000 ppm. This limit was exceeded in the headspace of all of the feed samples.

The Bacharach TLV was also used to measure concentrations of organics in the vent gas, feed tank headspace, and vapors above the bottoms when the sample pot was removed from the TFE. Measured organic concentration of the vent gas and feed tank headspace also exceeded the range of the instrument.

Samples of the TFE feed, bottoms, and condensate from selected tests were analyzed by a contract laboratory for volatile and semivolatile organics; percent oil, solids, and water; and metals using the EPA Contract Laboratory Program (CLP). The purpose of these analyses was to evaluate the process effectiveness on an individual component basis and to obtain information to calculate a material balance around the TFE.

RESULTS AND DISCUSSION

The feed rate and temperature of the TFE were varied over its normal range with no observed operational problems when operated at atmospheric pressure with the tested sludges. There were difficulties when it was operated under vacuum at 320 °C, as some carryover of feed into the condensate was observed. The condensate from the vacuum runs was a milky-white emulsion, which would require additional treatment to separate the oils.

When the TFE was operated at the 150 °C, some of the water in the feed was evaporated along with most of the VO. As illustrated in Table 2, the VO removals ranged between 99.5 and 99.8 percent at the low feed rate and decreased slightly when the feed rate was increased (98.6 to 99.8 percent at a feed rate of 154 lb/h). The bottoms temperatures for these runs were 98 to 102 °C, indicating that water was still boiling from the bottoms as it exited the base of the TFE.

The removal efficiency for volatiles was greater when the TFE was operated at higher temperatures. The VO removals when the TFE was operated at 320 °C were 99.88 to 99.99 percent, with no clear trends relative to changes in feed rate. These runs removed essentially all of the water and VO from the feed sludge, along with much of the higher boiling oils. The amount of bottoms sludge produced ranged between 10 and 13 percent of the feed rate, substantially reducing the amount of material requiring disposal. This bottoms product was a relatively viscous, high solids content sludge, which was still pumpable.

Several vacuum runs were performed with the TFE. These runs produced a milky-white emulsion as condensate, which contrasted substantially with the cleanly separating organic/aqueous condensate of the atmospheric pressure runs. A high-temperature vacuum run (320 °C) produced a bottoms product that was only 4.3 percent of the feed sludge. This indicates that a two-stage process (first-stage removal of water and volatiles at atmospheric pressure, second-stage removal of heavier oils under vacuum operation at high temperature) could be employed to reduce substantially the amount of sludge material requiring disposal.

Metals in the feed sludge appeared to remain in the bottoms products. Only minor amounts of metals were found in the organic condensate.

The organic condensates produced during the atmospheric pressure tests could easily be recycled as raw products to the refinery operation. This would reduce the actual operating costs of the TFE while removing organics from the wastes prior to disposal. The aqueous condensate was water saturated with the recovered organics and could be sent to existing wastewater treatment facilities at refineries. If the process is applied for the removal of volatiles only, the aqueous condensate could be recycled to the process feed, so that all water would exit with the process bottoms. (This would not be practical if large quantities of water were condensed, as in high-temperature operation) The bottoms sludge produced by the process could be treated by existing methods (land treatment) or perhaps incinerated. The

TABLE 2. TFE VO REMOVAL FOR SELECTED COMPOUNDS

	Operating Conditions		Reduction in concentrations from feed (%)[a]			
Test No.	Temperature (°C)	Flow rate (lb/hr)	Benzene	Toluene	Ethylbenzene	m-Xylene
5	150	71.6	99.58	99.61	99.48	99.54
7	150	153.7	99.73	99.78	98.83	98.64
8	310	68.5	99.72	99.84	99.68	99.67
10	310	143.4	99.76	99.90	99.78	99.75

[a] Based on GC/MS analyses.

ultimate treatment for any bottoms product will require additional testing of possible disposal methods.

The results from this test were used to verify a model that can be used to predict the effectiveness of TFE treatment on different waste sludges. Generally, a TFE is modeled as a one theoretical stage separation device. Countercurrent steam purging is thought to improve the separation to approximately one and one half theoretical stages. The number of theoretical stages, together with the partition coefficient (K) of the volatile organic component at the TFE operating temperatures, and the flow rates can be used to predict the percent removal of volatile organics from the sludge in a treatment device. For a complete discussion of the TFE model and the pilot test, the reader is referred to Harkins, Allen, and Northeim (1987) (1).

CONCLUSIONS

The TFE was found to have very high removal efficiencies of VO compounds from the waste sludges tested. In each of three methods used to assess the reduction of volatiles (two headspace analyses, one analysis of VO compounds in feed and bottoms), the removal efficiencies for VO compounds were greater than 99 percent.

REFERENCE

1. Harkins, S. M., C. C. Allen, and C. M. Northeim, 1987. Pilot-Scale Evaluation of a Thin-Film Evaporator for Volatile Organic Removal from Land Treatment Sludges. U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Alternatives Technology Division. (Draft. Prepared by the Research Triangle Institute under EPA Contract No. 68-02-3253, Work Assignment 1-6.)

U.S. ENVIRONMENTAL PROTECTION AGENCY HAZARDOUS WASTE CONTROL TECHNOLOGY DATA BASE

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) Hazardous Waste Control Technology Data Base was developed by the U.S. Department of Energy's Hazardous Waste Remedial Actions Program through a joint interagency agreement with EPA's Hazardous Waste Engineering Research Laboratory. The data base functions as an information resource on thermal treatment technology for handling hazardous wastes. It serves as a multifunctional information tool to support permit writers, researchers, private industry, and decision makers in managing, analyzing, and comparing similar waste components and technologies. The features of the data base incorporate (1) engineering data on permit applications for existing, new, and research development and demonstration facilities; (2) trial burn and design data; (3) on-line report generation capabilities; and (4) methods for conducting similarity analyses. Interactive menu-driven retrieval options have been designed to generate summary reports through selection of key parameters. The data base can be used to conduct similarity analyses of the data for (1) re-evaluating the technology data to compare with actual industry performance and operating conditions, (2) providing a reference guide to meet new and existing regulatory standards, and (3) providing a means of calculating the theoretical performance of trial burns. Overall, the data base functions as a means of tracking the status of permit applications, assists the decision makers in determining future research strategies, provides support data for public hearings on permit decisions, and supports EPA's regulatory standards and procedures. The scope of the data base is being expanded to incorporate technical data on chemical, physical, and biological treatment technologies.

ANALYSIS OF SAMPLES FROM THE GATEWAY NATIONAL RECREATION AREA AT JAMAICA BAY, NY

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The National Park Service (NPS) provided the Releases Control Branch (RCB) of the Hazardous Waste Engineering Research Laboratory with funding to perform a preliminary study of chemical pollutants entering the Jamaica Bay ecosystem at several designated sites near municipal landfills in Brooklyn, NY. The NPS needs this information to make an initial assessment of whether these landfills are potential contributing sources of pollution. The landfills will eventually be reclaimed by NPS as part of the Gateway National Recreation Area park system.

Bay samples were screened for the presence of priority pollutants. These samples were collected by NPS personnel at several sites near the landfills along the north shore of Jamaica Bay, NY and analyzed according to the requirements in 40 CFR Part 136 (Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule). The resulting data will be presented in this poster. In addition, the poster presents designated sampling sites on the bay and demonstrates the impact of pollution on the surrounding communities.

In the first part of the study (March 1985), appreciable concentrations of pollutants were found at the following levels: base/neutral and acid extractables (BNAs) 8-42 ppb (water), 300-9800 ppb (soil); polynuclear aromatic hydrocarbons (PAHs) 1.74 ppb (one water sample), 55.9-3515 ppb (soil); polychlorinated biphenyl (PCBs) aroclor 1260 5.45-43.2 ppb (soil); metals 0.11-6.41 ppm (water), 0.42-125 ppm (soil).

In the second part of the study (May-June 1986), appreciable amounts of base/neutral and acid extractables (BNAs) and metals were found in the landfill sediment samples, with the following ranges of maximum values: 495-6,740 ppb BNAs, 2.4-910 ppm metals. Aroclor 1260 was the only polychlorinated biphenyl (PCB) found in any of the samples (88.4 ppb in bay water and 128 ppb in sediment). Polynuclear aromatic hydrocarbons (PAHs) were found in both the bay water and sediment samples (5.16 ppb maximum); landfill samples were not analyzed for PAHs. In order to evaluate and document the quality of the analytical data generated, an extensive internal QA/QC program was followed, which will also be described in this poster.

CASE EVALUATIONS OF RD&D PERMIT APPLICATIONS

By

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The Environmental Protection Agency (EPA) is charged with regulating the incineration of hazardous waste under the Resources Conservation and Recovery Act (RCRA). Under current procedures the regional permit writer must make a number of engineering assessments during the course of the permit application concerning the adequacy of the design data, the consistency of the trial burn data, the appropriate limits to be set on operating conditions, and the parameters to be monitored to ensure continual compliance. A computer model has been developed to assessments, allowing them to perform fast and accurate energy and mass balance calculations for hazardous waste incinerators based on sound engineering principles. The mass balance is based on simple stoichiometric calculations assuming complete combustion. The energy balance solves for gas temperature, wall temperature, and shell temperature considering chemical heat, heat of vaporization, sensible heat, radiation, convection, and conduction. this procedure can be useful to incinerator designers and operators and especially to permit writers. Permit writers can use the procedure to evaluate the feasibility of incinerator designs and concepts, to issue research, development and demonstration (RD&D) or construction permits and to evaluate the consistency of trial burn measurements and set appropriate operating limits on the basis of those measurements for operating permist of hazardous waste incinerators. The procedure has been used to evaluate an actual RD&D permit application by Waste-Tech Services, Inc. for a fluidized bed incineration system. The incinerator is predicted to be capable of achieving the times, temperatures, and velocities claimed in the permit application, and incinerator performance is predicted to be most sensitive to changes in air flow; waste feed, waste heating value, and auxiliary fuel flow.

OVERVIEW: EPA's MOBILE INCINERATION SYSTEM AND TRANSPORTABLE INCINERATION

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Over the past five years, the EPA mobile incineration system has been successfully tested using PCB-contaminated liquids and dioxin-contaminated liquids and solids. A field demonstration on a variety of dioxin-contaminated liquids and solids was conducted between July 1985 and February 1986. A total of 2,000,000 lb of solids and 180,000 lb of liquids were successfully decontaminated during that time. Subsequently, four design modifications have been made to improve throughput capacity and availability.

The modifications include changes to the ram feed system, the addition of an oxygen enrichment system in the kiln, installation of a cyclone between the kiln, and secondary combustion chamber (SCC), and installation of a wet electrostatic precipitator downstream of the SCC. Key design features of these modifications and their potential benefit to performance and operating costs will be discussed. Updated operational data will be presented as available.

This presentation will also discuss conceptual configurations of a transportable incineration system that has a thermal duty of 75 million Btu/hr. Cost estimates of a truck-mounted transportable incineration system will be described.

BOILER COFIRING OF CHLORINATED HYDROCARBONS

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ABSTRACT

An in-house project to study the destruction of liquid hazardous waste by cofiring in an industrial package boiler has recently been completed. The test facility consisted of a 2.5 million Btu per hour North American Scotch Marine boiler, a surrogate hazardous liquid feed system, a mini-VOST sampling train, and a continuous emissions monitoring system (CEMS). Hazardous wastes were simulated by mixing NO. 2 fuel oil with carbon tetrachloride, monochlorobenzene, and perchloroethylene. Each of these principal organic hazardous compound (POHC) surrogates constituted 2% by weight of the mixture. This mixture was cofired with natural gas in the boiler. The overall program objective was to define the envelope of operating conditions where a 99.99% or greater destruction and removal efficiency (DRE) could be achieved for the POHC. Waste surrogate and fuel (natural gas) were cofired under both steady state and transient conditions. Boiler load, stoichiometry, waste heat percent, and degree of atomization were varied under steady state conditions, while load ramp up/down, stoichiometric fluctuations, and waste feed rate fluctuations were the parameters evaluated under transient conditions. Stack emissions of NO_x, CO, HC, and oxygen were measured by CEMS, while chlorinated POHCs were sampled with the mini-VOST train and analyzed using a GC (Hall detector). Samples of the waste mixture and internal boiler deposits were also collected. Indications from the results are that less than 99.99% DRE was experienced with a boiler stoichiometry near 1.0, a high firing rate (80%), and 50% waste heat input under both good and bad atomization conditions. A DRE less than 99.99% resulted under transient conditions of load ramp up/down, stoichiometry fluctuation, and waste feed rate fluctuation. Monochlorobenzene is the most difficult of the tested compounds to destroy, indicating that aromatic chlorohydrocarbons could be the major concern in cofiring. Steady, moderate boiler operating conditions give the best assurance of maintaining 99.99% DRE.

DEMONSTRATION, TESTING, AND EVALUATION OF COMMERICAL TECHNOLOGIES UNDER THE SITE PROGRAM

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The Superfund Innovative Technology Evaluation (SITE) Program provides a mechanism by which the US EPA can cooperate with the private sector in maximizing the use of innovative remediation technologies.

The SITE Program provides certain support and financial assistance for the development and demonstration of promising technologies, thus enhancing their establishment and availability.

The poster describes some technologies currently being examined under the program. They include: the International Waste Technologies solidification process, which will be demonstrated on PCB-contaminated soil in Hialeah, Florida; the Westinghouse plasma arc process that will be tested at Love Canal; and the Shirco incinerator planned for a demonstration at Tampa, Florida.

CONDITIONS WHICH ENHANCE BIODEGRADATION OF ORGANIC COMPOUNDS BY WHITE ROT FUNGI

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ABSTRACT

The white rot fungus *Phanerochaete chrysosporium* is able to degrade a broad spectrum of typically hard-to-degrade environmental pollutants. The present study focused on culture conditions that enhance the mineralization of environmental pollutants. Special attention was given to the use of inexpensive carbohydrate sources to develop a useful and economically practical waste treatment system. The initial rate of mineralization of ^{14}C-DDT, which was used as a model organopollutant, was linear (i.e., first order) with respect to ^{14}C-DDT concentration. Cultures containing one percent glucose, starch, or cellulose mineralized 14.5%, 25.1%, and 32.1%, respectively, of the ^{14}C-DDT during a 90 day incubation period. No significant difference in the initial rate of ^{14}C-DDT mineralization was observed. However, mineralization was minimal after 18 days of growth on glucose, but continued at substantial rates in cultures in which cellulose or starch served as the carbohydrate source. Cultures grown on used newspaper, wheat straw, or corn cobs mineralized 8.1%, 13.3%, and 8.2%, respectively, of the ^{14}C-DDT during 30 days of incubation. In other studies it was shown that 42% of the ^{14}C-DDT initially present was mineralized in 60 days in culture in a medium composed of (1:7.5 w/v) horse manure liquor, 8% cellulose and 2.5% glucose. The rate and extent of ^{14}C-DDT mineralization was also found to be affected by the concentration of trace minerals. For example, a twenty-fold increase (from 0.004 uM to 0.08 uM) in the concentration of $FeSO_4$ resulted in a two-fold increase in the amount of ^{14}C-DDT mineralized. Similar effects were observed when the concentrations of $CuSO_4$, $ZnSO_4$, and $MnSO_4$ were varied. These studies demonstrated that it is possible to substantially increase the rate and extent of xenobiotic degradation by *P. chrysosporium*. They further suggest that it may be possible to develop an efficient and economical waste treatment system based on the use of this microorganism. (Supported by USEPA Cooperative Agreement CR811464).

DEMONSTRATION AND EVALUATION OF THE EPA MOBILE CARBON REGENERATOR

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This poster presents information on the EPA Mobile Carbon Regenerator, which was developed as part of EPA's overall mission to actively encourage the use of cost-effective, advanced technologies during cleanup operations. Specifically, the regenerator is intended to provide on-site reactivation of granular activated carbon (GAC) used to adsorb contaminants at Superfund sites. The regenerator consists of a rotary kiln with afterburner, scrubber, and auxiliary equipment mounted on a semi-trailer, and is capable of regenerating up to 100 lb/hr (dry basis) of carbon. Automated feed- and product- handling systems were added during the current phase of system development.

Most recently, the regenerator was run in a demonstration operation using GAC from the Stringfellow hazardous waste site, Riverside County, CA. Results of this operation are presented, together with the results of a previous operation using GAC spiked with tetrachloroethylene and with ortho-dichlorobenzene.

PRETREATMENT OF LAND-TREATED WASTES

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ABSTRACT

The purpose of this project is to investigate hazardous waste dewatering at petroleum refineries to evaluate air emissions associated with this pretreatment operation. Refineries routinely dewater API sludges and dissolved air flotation (DAF) float prior to disposing of this material. The sludge from these dewatering operations is a listed hazardous waste and is typically either land-treated or disposed of in a hazardous waste disposal facility.

Specifically, this project determined the fate of both semivolatile and volatile organic carbon during the dewatering operation. By reviewing existing data, the different types of dewatering equipment used in this operation were identified. Several refineries were visited and a refinery using a belt filter press was selected for testing. The refinery processed API and DAF sludge separately (most refineries mix these sludges prior to dewatering). The facility had a forced draft ventilation system which made it possible to test air emissions from the belt filter through an exhaust stack.

Two days of testing were conducted, one day while API sludge was being processed and a second day while DAF float was being dewatered. Each test ran for six hours. During the test, inlet and outlet streams to the filter were measured and sampled hourly along with testing to quantify volatile and semi-volatile organics in the air vented from the filter building.

The samples were analyzed for 13 specific organic compounds, as well as purgible and non-purgible organic carbon. Solid, oil and water content of each stream was also analyzed. Data taken during the test were used to quantify the flows in and out of the filter, and a material balance was done as a cross-check on the accuracy of our data. The results of the sampling and analysis effort were used to determine the fate of the organics and determine the level of air emissions generated from this type of operation.

GEOTECHNICAL ANALYSIS FOR REVIEW OF DIKE STABILITY

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ABSTRACT

The structure and capabilities of a user-friendly, interactive computer program developed for the stability analysis of dikes (GARDS) are described. The GARDS program is designed to guide the geotechnical user through the customary steps of earth dike analysis. The significant difference between GARDS and other stability programs commonly available is the opportunity to perform all of the following analyses in a single package: automatic search to determine the critical failure surface for both rotational (slip circle) and translational (wedge) stability analyses; automatic search to locate zones of greatest liquefaction potential and to compute total and differential settlements of foundation soils; finite element hydraulic analysis to determine the steady state piezometric surface through the section (including the case of an impermeable barrier such as a clay liner); evaluation of excess pore pressure conditions produced by confined steady state flow and potential slope stability and uplift conditions resulting therefrom; determine the maximum exit gradient and the potential for piping failure.

The program was developed under the the sponsorship of the U.S. Environmental Protection Agency and therefore emphasizes hazardous waste applications although it is suitable for general use. The GARDS package is designed for use on the IBM/PC/XT microcomputer. Documentation consists of a technical users maunal which presents basic theory, program operational procedures, and example computer solutions.

LAND BAN DATA NEEDS

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ABSTRACT

All of the RCRA hazardous wastes listed as of November 8, 1984 were ranked by their intrinsic hazards and their volumes, and a time frame was established for conditional land disposal restrictions. The EPA will obtain data on the operation and performance of demonstrated, available treatment technologies for these hazardous wastes. The HWERL sampling and analysis program is described.

DEMONSTRATE COMPUTER ASSISTED ENGINEERING (CAE) TECHNIQUES FOR REMEDIAL ACTION ASSESSMENT

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ABSTRACT

Computer Assisted Engineering (CAE) refers to a broad range of powerful software tool packages which aid engineers primarily in the fields of machine design, microelectronic circuit design and structural design. Since powerful personal computers are becoming widely available, CAE systems using these computers are being developed to assist with many other types of engineering problems.

A CAE system customized for remedial action assessment will be developed by integrating several existing software packages, including a Computer Aided Design/Drafting (CADD) package, a Geographic Information System (GIS), and a groundwater modeling package. The resulting system will be demonstrated by applying it to evaluation of remedial action alternatives at a Superfund site.

HAZARDOUS WASTE RESIDUALS CHARACTERIZATION

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The Office of Solid Waste and Emergency Response is establishing regulations for the disposal of waste or residue into the land. In the development of these regulations, an evaluation of several hazardous waste treatment techniques was made at selected field sites. This presentation summarizes the results of these evaluations with respect to the characterization of treatment residuals and their suitability for disposal to the land. Included in this presentation, where data is available, is a summary of the results from the application of the Toxicity Characteristic Leaching Procedures (TCLP) on treatment residuals. Also discussed will be the Paint Filter Test and Liquid Release Test, however, primary emphasis will be placed on a discussion of the TCLP. The TCLP, the Paint Filter Test, and the Liquid Release Test are three criteria proposed to be used by the U.S. Enviromental Protection Agency to regulate disposal of hazardous waste residuals to the land on a pass/fail basis.

COST ENGINEERING MODELS FOR REMEDIAL RESPONSE TECHNOLOGIES

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ABSTRACT

The purpose of this project was to develop a cost estimation model for remediation technologies at hazardous waste sites. The work was conducted for the U.S. Environmental Protection Agency (EPA), Hazardous Waste Engineering Research Laboratory in cooperation with the Office of Emergency and Remedial Response. The model is designed for operation on a personal computer and can provide levels of detail in the estimate commensurate with the detail of input parameters available, i.e., the stage of design.

The cost estimation model takes into account variations in site characteristics, waste quantities, worker safety requirements, and regional costs. Output formats and types of cost calculations are consistent with the EPA Remedial Action Costing Procedures Manual. Default values for interest rates, discount rates, planned life, contingency allowances, etc. are consistent with the costing procedures manual.

The model can be used by Federal or State government and contractors (REM/FIT Contractors, cleanup contractors, etc.) for quick and effective calculations of costs for evaluating and comparing a variety of different cleanup or remediation alternatives.

TRIAL BURN MEASUREMENT GUIDANCE

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ABSTRACT

The Resource Conservation and Recovery Act (RCRA) requires the U.S. Environmental Protection Agency (EPA) to develop, promulgate, and implement regulations which control the generation transportation, treatment, storage, and disposal (TSD) of hazardous wastes. An integral part of these activities is reviewing and issuing permits to hazardous waste incineration (HWI) facilities.

The performance of HWI facilities is evaluated by conducting a "Trial Burn" during which measurements are made on the various input and output streams to the incinerator. In this presentation, the measurement aspects of a trial burn are reviewed. The review is oriented towards how the measurements are made. The major elements of incineration measurements related to the process monitoring, sampling, and analysis aspects of trial burns are discussed. Measurements reviewed will include volatile and semivolatile Principal Organic Hazardous Constituents (POHCs) and Carbon Monoxide (CO). A Volatile Organic Sampling Train (VOST) will be demonstrated.

MICROSCOPIC AND MICROCHEMICAL ANALYSES OF SOLIDIFIED INORGANIC WASTES CONTAINING INTERFERENCE COMPOUNDS

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Solidification/stabilization processes are thought to be affected by the presence of certain interference compounds. The mechanism of interference is unknown but is believed to involve the microscopic phases which are normally formed during hydration of the pozzolanic matrix materials. Recent studies, for example, have characterized the interaction between selected organic wastes and portland cement and have shown that set retardation results from an alteration of the chemical and morphological structure of the calcium silicate hydrates that normally impart structural integrity to the hardened paste.

The present study is an attempt to determine if inorganic wastes (interferences) have the same detrimental effect upon similarly solidified inorganic sludges. X-ray powder diffraction is used to identify the crystalline phases which differ in chemical composition or amount from those contained in sludge solidified in the absence of interference compounds. Scanning electron microscopy is used to characterize the morphology and to identify the form of the important phases. The experimental results are described and their importance to the design of effective solidification schemes is discussed.

VACUUM-ASSISTED IN-SITU STEAM STRIPPING
TO REMOVE POLLUTANTS FROM CONTAMINATED SOIL

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ABSTRACT

A long term project has recently been initiated (Fall 1986) by Drexel University, under the sponsorship of the U. S. Environmental Protection Agency, to develope the means by which to steam strip (distill) pollutants from contaminated soils.

The overall project is divided into four phases:

Phase I - Perform literature and information search and design of small scale laboratory experiments.

Phase II - Run small scale laboratory experiments to determine the feasibility of steam stripping of a wide range of chemicals for pertinent soil types and their different conditions.

Phase III - Design and perform small pilot scale steam stripping and vacuum entrapment experiments on selected chemical/soil combinations.

Phase IV - Perform final design of field unit. Possible supervision of the construction of a field deployable unit working closely with EPA-Edison personnel.

Although a great deal of chemistry and chemical engineering literature is available as regards steam stripping and steam distillation, there is virtually no literature concerning the interaction of steam with soils. Thus the preliminary work has involved simple experiments to develope basic knowledge in this area.

The volume expansion of a variety of soil types exposed to steam (at about 100°C and one atmospheric pressure) in an autoclave is discussed. Also the behavior of a steam front (injected at 100°C and 5 psi) in a soil-filled, thin transparent box will be presented. From these steam front movements, effective permeabilities for steam movement are derived and compared with water permeabilities.

Containment of the stripped waste is an absolutely essential aspect of the work. Our geosynthetic containment system is of a unique design, and some preliminary results with this containment system are given.

USE OF MODIFIED CLAYS FOR ADSORPTION AND CATALYTIC DESTRUCTION OF CONTAMINANTS

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and

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ABSTRACT

The unique properties of smectite clays that are important in designing effective adsorbents and catalysts are (1) high surface area (2) high cation exchange capacity (3) swelling properties of the clay platelets and (4) high surface acidity and reactivity. Such properties make these materials inherently reactive and allows tremendous synthetic versatility to produce structures having specific properties for detoxication. Our goal is to develop a process for treating liquid wastes in which the contaminant is first immobilized on the clay material and then detoxified via catalysis on the clay surface. The clay-based materials being developed for this purpose are (1) transition metal saturated clays (2) organo-clays (3) pillared clays and (4) delaminated clays. The metal clays are versatile catalysts which can be used to form reactive radical cations of organic toxicants such as dioxins and chlorophenols. These reactive radical species are subject to a variety of potential reactions to form less toxic products. Important reactions such as polymerization and dechlorination have been achieved. Organic cations can also be placed on the surface of smectite clays to impart hydrophobic properties important for adsorption of trace organic contaminants from aqueous streams. Pillared and delaminated clays are microporous to macroporous derivatives formed by the reaction of natural clays with robust polyoxocations. The relatively large pore sizes of these clays make them ideal adsorbents for large chlorinated hydrocarbons. Also, metal catalysts can be introduced into their structures to facilitate subsequent oxidation of the adsorbed toxicant.

STRINGFELLOW LEACHATE TREATMENT WITH A ROTATING BIOLOGICAL CONTACTOR

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ABSTRACT

A study was conducted with a rotating biological contactor (RBC) for treatment of leachate from the Stringfellow hazardous waste site in Riverside County, California. The leachate was transported from California to Cincinnati, where a pilot sized RBC was installed at the U.S. EPA's Testing and Evaluation (T&E) Facility.

A series of kinetic runs were made with primary effluent from the City of Cincinnati's Mill Creek Sewage Treatment Plant to develop the biomass on disks and to obtain a standard kinetic removal rate. These runs were then followed with Stringfellow leachate experiments that included

- Operations at various ratios of leachate to primary effluent
- Operations at 100% leachate
- Operations to increase the percentage removal of dissolved organics.

This poster presentation reports on the results from these experiments and the effectiveness of an RBC to adequately treat leachate from the Stringfellow hazardous waste site.

SEPARATION AND RECOVERY OF HAZARDOUS WASTES

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ABSTRACT

Two projects at the Illinois Institute of Technology that are currently supporting the basic research activities of EPA involve multi-component adsorption mechanisms and metals speciation and precipitation processes. These two pieces of work are intended to extend the basic understanding of separation and recovery technologies which are vital to the current legislation controlling hazardous waste generation, treatment and disposal.

The first project, dealing with organic pollutant separation and recovery, has concentrated on the dynamics of multi-component adsorption/desorption systems. The kinetic data and isotherm parameters obtained from a series of experiments with a quartz spring apparatus have been used to develop computer models of multi-component adsorption in air and in water. Preliminary tests in long column adsorption experiments are in good agreement with both models.

The second project, also investigating a separation process, has focused on metal speciation and precipitation phenomena. The soluble phase kinetics of metal reactions in both single ligand and competitive ligand systems have been evaluated and reaction orders and rate constants have been proposed for several systems. In addition, the effects of reaction stoichiometry and reactor hydraulic regime on the onset of nucleation and precipitation have been studied. The resulting precipitates have been characterized with respect to their composition, morphology, and surface charge.

TREATMENT OF AQUEOUS METAL AND CYANIDE BEARING HAZARDOUS WASTES

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ABSTRACT

With the amendment of the Resource Conservation and Recovery Act (RCRA) by the Hazardous and Solids Waste Amendments (HSWA) and the resulting restrictions on land disposal of hazardous wastes, the US Environmental Protection Agency is assessing technologies that can be substitutes for, or precursors to land disposal. This paper describes the research work being conducted at the EPA's Test and Evaluation Facility in Cincinnati, Ohio, involving treatment of electroplating and metal finishing hazardous wastewater.

A series of treatment units has been designed and fabricated to determine the optimum combination of the units for any given waste. These units are: lime precipitation, flocculation, clarification, mixed-media filtration, sulfide precipitation, activated carbon adsorption, ion exchange and alkaline chlorination of cyanide. All of these units except alkaline chlorination of cyanide have been tested with industrial metal bearing wastes (EPA RCRA codes D006/D008) in the first experimental phase. A process flow rate of 2.5 gallons per minute was used during these test runs and a total of 450 gallons of waste was treated in each run. Ion exchange was found to be a promising polishing technology.

In the second experimental phase, the alkaline chlorination of cyanide will be tested after the necessary safety features are incorporated into the system. The system will be modified to operate at a lower flow rate of 1.0 gallons per minute to reduce the amount of hazardous waste that has to be imported and handled during each run. Plans for utilizing additional treatment units (chromium reduction, stabilization/fixation of precipitated sludges) will also be presented.

AN EXPERIMENTAL INVESTIGATION OF SINGLE DROPLET COMBUSTION OF CHLORINATED HYDROCARBONS

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ABSTRACT

Experiments have been conducted with chlorinated hydrocarbons to investigate the combustion characteristics of liquid hazardous wastes. In this study, the combustion and vaporization of single droplets of pure chlorinated hydrocarbons were examined and the effect of adding hydrocarbons to the chlorinated hydrocarbon to facilitate burning was investigated. Single droplets were produced by a piezoelectric generator, injected into a hot chamber, and sized by microphotography. In addition, the liquid phase history of the droplet was determined using phase discriminated sampling and GC analysis. The size history of the droplets was used to generate D^2-Law plots from which burning rate parameters were extracted. Evidence of droplet extinction appeared on D^2-Law plots for certain mixtures of chlorinated and non-chlorinated hydrocarbons. From this study, the effects of chlorine loading, volatility differentials in mixtures, and mixture percentage in single droplet combustion and vaporization are presented. The implications of these effects on the behavior of full scale hazardous waste incinerators are discussed.

CATALYTIC DESTRUCTION OF HALOGENATED HAZARDOUS WASTE

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ABSTRACT

Disposal of halogenated wastes using methods of catalytic oxidation is being evaluated from both technology and economic standpoints. Vapor phase oxidation of halogenated compounds over supported transition metal oxides shows substantial reactivity at temperatures well below those necessary for homogeneous reaction. The spectrum of oxidation products obtained depends strongly on the choice of catalyst and the molecular makeup of the halogenated species along with any other molecules present in the vapor phase.

Catalyst deactivation and corrosion of the support system are important design considerations based on the quantities of halogen-acids formed during the oxidation process. Screening of both catalysts and supports has yielded several systems capable of withstanding reactor conditions.

Although considerable research remains to be done, the underlying flexibility of the catalytic process makes it a potentially viable method for treatment of halogenated wastes.

EXPERT SYSTEM SCREENING OF REMEDIAL ACTION TECHNOLOGIES FOR CERCLA SITES

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ABSTRACT

A prototype computerized expert system called TECHSCRN has been developed for identifying hazardous waste cleanup, control, and treatment technologies that would be feasible to apply at Superfund remedial action sites. The system matches characteristics of the site and of the materials being released against the conditions under which a particular type of technology is applicable. This initial screening produces a more manageable list of action alternatives that can then be subjected to more detailed study. The knowledge base for this system is being acquired primarily from existing literature sources. The prototype system has been coded in the PROLOG language and operates on a personal computer. The system can function as both a site-specific screening tool and as a general purpose data base system on remedial action technology characteristics. Information on 30 different types of containment and removal technologies is currently available. This knowledge base is being expanded to include treatment technologies as well. Future plans call for adding a design capability to the system that combines individual technologies into overall system alternatives as well as a cost estimating capability to provide a better basis for screening of alternatives. A hands-on demonstration of TECHSCRN will be provided.

ACTIVITIES AT LOUISIANA STATE UNIVERSITY'S HAZARDOUS WASTE RESEARCH CENTER

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ABSTRACT

The Hazardous Waste Research Center at Louisiana State University (LSU) is conducting fundamental and exploratory research in these general areas: environmental media/waste interaction, incineration, and alternative methods of treatment/destruction. Although administered through LSU's College of Engineering, individual research projects are being conducted by multi-disciplinary groups representing a number of academic departments. Ongoing research projects for 1987 are:

. A Study of Immobilization Mechanisms In Solidification/Stabilization Using Cement/Silicate Fixing Agents.

. Incineration of Liquid Hazardous Waste Droplets.

. An Indepth Investigation of Rotary Kiln Incineration Performance.

. Supercritical Extraction and Catalytic Oxidation of Toxic Organics from Soil.

. Short Range Air Dispersion of Toxics from Area Sources.

. Detoxification of Dioxin contaminated Sludges Using Combined Microbiological and Photolytic Degradative Approaches.

Quickening regulatory requirements imposed on the hazardous waste industry have resulted in the Center's responding to industry needs by implementing in 1985 the Industry Associates Program. Through this program Center resources and research finding are being applied to current industrial problems in hazardous waste treatment and disposal. One of the first projects conducted under this program is "Fate and Transport of Hazardous Materials After Deep Well Disposal". The purpose of this research is to determine whether interactions occur between specific hazardous waste materials and disposal formation rock matrices or impurities within a rock matrix.

Partitioning of PCDDs and PCDFs in Soils Containing Wood Preservative Fluid

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Polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are found in significant concentrations in some wood treatment fluids containing the active ingredient pentachlorophenol (PCP). Surface and subsurface soils of many facilities using the PCP process have been contaminated with PCDDs and PCDFs. This contamination has resulted primarily from spillages related to retort operation and seepage from unlined surface impoundments containing waste waters.

The U.S. EPA is investigating factors contributing to soil migration of PCDDs and PCDFs at wood treatment facilities in order to better assess clean-up options and prevent future subsurface contamination. The objectives of this project are to (1) examine partitioning of PCDDs and PCDFs in soils contaminated with wood treatment fluid containing PCP and, (2) develop a laboratory method which can be used to assess potential mobility of PCDDs and PCDFs on a site-specific basis.

Results of this investigation to date indicate that soils contaminated with PCP wood treatment fluid contain primarily hexa through octa cogeners of PCDD and PCDF. Initial findings indicate that PCDDs and PCDFs are partitioned onto soil contaminated with wood treatment fluid to a far lesser extent than would be expected if these compounds were partitioned onto soil not containing wood treatment fluid.

TECHNICAL RESOURCE DOCUMENTS

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ABSTRACT

The Hazardous Waste Engineering Research Laboratory has produced a series of five large reports that compile technical information about alternative treatment and destruction processes for various hazardous waste streams. Each of the reports is devoted to one of the high priority hazardous waste streams being evaluated by the EPA for land disposal prohibition regulations i.e., waste streams containing dioxins, solvents, corrosives, halogenated organics, and metals/cyanides.

The reports provide information that can be used by environmental regulatory agencies and others as a source of technical information describing waste management options to land disposal. These options include waste minimization (i.e., source reduction, reuse, and recycling), treatment, and disposal of contaminants in waste streams. Although emphasis is placed on the collection and interpretation of performance data for proven technologies, other potentially applicable waste minimization processes and treatment/recovery technologies are also addressed. All options are described in terms of their actual performance in removing constituents of concern, their associated process residuals and emissions, and those restrictive waste characteristics impacting the ability of a technology to effectively treat the wastes under consideration. Cost and capacity data are also provided to help assess the applicability of the technologies to specific waste streams.

OXIDATION OF PERSISTENT AROMATIC POLLUTANTS BY LIGNIN-DEGRADING ENZYMES

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ABSTRACT

The ligninase of the wood-rotting fungus, Phanerochaete chrysosporium, catalyzes the oxidation of a variety of lignin-related compounds. This enzyme also catalyzes the oxidation of certain aromatic pollutants and compounds related to them. Polycyclic aromatic hydrocarbons with ionization potentials less than *ca*. 7.55 eV, are oxidized to quinones, with the source of the quinone oxygens being water. A related enzyme, horseradish peroxidase, is known to oxidize only those polycyclic aromatic hydrocarbons that have ionization potentials less than *ca*. 7.35 eV, *i.e*. ligninase is the more oxidizing of the two peroxidases. Ligninase also oxidizes chlorophenols and certain halogenated anisoles. In the case of 2,4,6-trichlorophenol, the reaction proceeds with dechlorination at the 4-position to yield 2,6-dichloro-p-benzoquinone as the product. as determined by gas chromatography/mass spectrometry analysis. Certain dibenzo(p)dioxins are also substrates for ligninase, and the visible and electron spin resonance spectra of reactions in progress show that substrate cation radicals are intermediates in catalysis.

LABORATORY STUDY OF THE THERMAL DECOMPOSITION OF SULFUR HEXAFLUORIDE

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ABSTRACT

This report presents the results of a laboratory evaluation of the gas-phase thermal decomposition of sulfur hexafluoride (SF_6). Thermal decomposition profiles were generated for pure SF_6 and SF_6 doped in a mixture containing carbon tetrachloride (CCl_4), tetrachloroethylene (C_2Cl_4), 1,2,4-trichlorobenzene (TCB), and toluene (C_7H_8). The data were generated in both oxidative and near-pyrolytic atmospheres with the residence time for reaction held at 2.0 seconds.

Thermal decomposition profiles for pure SF_6 as a function of reaction atmosphere indicate that SF_6 is an extremely stable material with an extrapolated temperature for 99.99% destruction much greater than 1050°C. The data also indicate no substantial effect of SF_6 stability on oxygen concentration. Thermal decompositon profiles for the SF_6 mixture components evaluated under oxidative reaction conditions indicate that although SF_6 begins to degrade at a temperature of 500°C, its stability decreases slowly at higher temperatures. The remaining mixture components exhibit rapid oxidative degradation above temperatures of 500°C. As a result, SF_6 is the most stable component in the mixture by far with an extrapolated temperature for 99.99% destruction much greater than 1050°C. Similar profiles for the SF_6 mixture constituents evaluated under near-pyrolytic reactor conditions indicate that SF_6 is the most stable component in the mixture by far with an extrapolated temperature for 99.99% destruction much greater than 1050°C.

Considerations of the molecular structure (S-F bond dissociation energy ~90 kcal/mole) are consistent with the experimental results. Measurements of SF_6-OH radical reactivity in this laboratory indicate very low reaction cross-sections. This finding is consistent with SF_6's approximate zeroeth-order decomposition behavior with respect to oxygen concentration. In addition, comparison of SF_6 unimolecular decomposition as calculated via RRKM theory is in good agreement with the pure compound experimental data.

A major application of this study is the use of SF_6 as a surrogate to monitor hazardous waste incinerator performance as defined by current regulations for principal organic hazardous constituent (POHC) destructability. Two major requirements of an ideal surrogate are high thermal stability (relative to hazardous constituents in the feed), and the ability of the surrogate to "track" hazardous consitiuent destruction. With respect to these requirements, this laboratory evaluation has shown that measurement of effluent SF_6 concentration may represent an accurate measure of incinerator performance. Field studies have confirmed this hypothesis as 99.9% DRE of SF_6 has resulted in 99.999% (destruction limit 99.9999%) DRE of CCl_4, C_2Cl_4, TCB, or any known hazardous waste constituent.

Areas of additional study include evaluation of the relationship between SF_6 and products of incomplete combustion (PICs) thermal stability. This is important because previous studies of POHC degradation indicate much higher stability for thermal reaction products, especially under near-pyrolytic conditions.

THE U.S. EPA COMBUSTION RESEARCH FACILITY

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In the past year, three major incineration test programs have been completed at EPA's Combustion Research Facility (CRF). The first consisted of incinerating a synthetic waste comprised of distilled fuel oil containing 30 percent PCB-1260 in the CRF liquid injection incineration system (LIS). The second test program consisted of incinerability testing of four wastes being generated through remediation of the Bridgeport Rental and Oil Services (BROS) Superfund site in Bridgeport, New Jersey. The third program investigates the fate of trace elements fed to an incinerator as a function of feed composition and the incinerator temperature and excess air level. Results from these tests are abstracted in this poster (the BROS test and the LIS trace element tests are discussed in other papers in the symposium).

CONSTRUCTION AND SHAKE DOWN OF AN ENVIRONMENTAL TESTING CHAMBER FOR SOIL REAGENT RESEARCH

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Chemical and biochemical means to detoxify soil are becoming more prominent in the arsenal of treatment technologies for the detoxification of soil contaminated with hazardous waste. Due to permitting restrictions and the lack of controlled field conditions, the application of these new technologies to actual field sites continues to be throttled. The Environmental Testing Chamber (ETC) has been assembled to alleviate some of these difficulties. At this stage of investigation, the chamber is currently built and awaiting more auxillary equipment in order to begin shake down and testing to determine design performance. It is designed as a generic device, that can study chemical, biological, physical and engineering design aspects of hazardous waste treatment technologies. This testing chamber will give a better assessment of the treatability of a technology at this intermediate scale. The loss of contamination is best partitioned into the various environmental and treatment process parts affecting the hazardous waste site. The Environmental Testing Chamber will permit the allocation of contaminant losses to the various major contributors to the overall loss.

The main objectives of the ETC research are: 1) close simulation of field conditions; 2) improved control of treatment technology; 3) engineer treatment optimization; 4) enhance scale-up assessment; 5) provide cost-effectiveness treatment design; 6) access to all contaminated media in the chamber; 7) complete controls of contaminant losses. The planned future developments of the chamber include additional aspects to more completely simulate the real world such as microclimatology and weathering. Also, to develop additional prototype chambers, as necessary, to study other treatment processes and environmental settings. Other possible chamber design changes may include: 1) rainfall simulation; 2) photolytic decomposition reactions; and 3) surface and subsurface waterflow as it affects the treatment process.

EARTHEN LINERS: PROTOTYPE PHASE OF A FIELD STUDY OF TRANSIT TIME

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ABSTRACT

In the first phase of a project to determine transit times of water and solute through a partially-saturated field-scale earthen liner, a prototype clay liner (10x30x3 feet) was constructed. The main goal of the prototype was to determine if desired moisture, density, and hydraulic conductivity relations could be achieved in the field using the selected clay material (Batestown Till) and full-size compaction equipment. Specifically, the prototype was necessary to determine if the U.S. EPA hydraulic conductivity criterion of less than 1×10^{-7} cm/s for earthen liners could be met at the study site. Additional goals were to test instrument installation techniques and provide undisturbed samples of liner materials.

In-situ prototype infiltration rates were measured using two large (5' inner ring diam.) double-ring infiltrometers. Apparent steady-state flux of 1.5×10^{-7} cm/s was achieved after about 3 weeks. Similar rates (2×10^{-7} cm/s) were obtained from three smaller infiltrometers (8" inner ring diam.). Results suggest that the prototype met the low hydraulic conductivity requirement.

Rhodamine and fluorescein were placed in the inner and outer rings, respectively, of one of the large infiltrometers to indicate possible preferential flow pathways. Dye patterns observed during excavation indicated that some lateral flow occurred between lift interfaces. Although the performance criterion was met, the dye experiments show a need for better lift bonding.

Morphological study of two prototype profiles revealed variation in the degree of compaction within lifts. Thinner lifts or longer compactor feet are expected to improve compaction uniformity and lift bonding.

A combination of vertically and horizontally installed tensiometers, gypsum blocks, neutron access tubes, and lysimeters were used to monitor moisture and dye movement. Instruments worked in either orientation (except lateral neutron access tubes which were damaged during construction). However, the horizontal instruments were necessarily installed at lift interfaces which may be preferential flow paths. In addition, horizontal instruments may be destroyed if the lift thickness is decreased. Vertical installations showed no evidence of channeling and were deemed more satisfactory than horizontal ones.

The next phase of the project is to build a large clay liner (30x60x3 feet) for long-term monitoring of ponded water and tracers.

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